

FILE 'CAPLUS' ENTERED AT 08:59:30 ON 13 DEC 2002
L71 72 S L68 AND SILIC?
L72 20 S L68 NOT L71

=> s l2 and zeolite
4275 L2
78216 ZEOLITE
78017 ZEOLITES
94194 ZEOLITE
(ZEOLITE OR ZEOLITES)
L73 5 L2 AND ZEOLITE

=> d ibib abs hitstr 1-5

L73 ANSWER 1 OF 5 CAPLUS COPYRIGHT 2002 ACS
ACCESSION NUMBER: 2002:492041 CAPLUS
DOCUMENT NUMBER: 137:59001
TITLE: Agricultural chemical preparation in a pile type using
absorbent minerals or natural organic matters as a
carrier and its use
INVENTOR(S): Yoon, Ji Hyun
PATENT ASSIGNEE(S): S. Korea
SOURCE: Repub. Korean Kongkae Taeho Kongbo, No pp. given
CODEN: KRXXA7
DOCUMENT TYPE: Patent
LANGUAGE: Korean
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

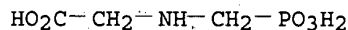
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	KR 2000073278	A	20001205	KR 1999-16482	19990508
AB	An agricultural chem. prepn. in a pile type as a carrier is prepd. by mixing agricultural chems. with absorbent minerals or natural org. matters, and then extrusion molding a cylinder of 1-20 mm thickness, and then sharpening the end of the cylinder. The absorbent minerals are chosen from zeolite, plastic diatomite, plastic white clay, kaolinite, bentonite, diatomite, or clay. The carrier contains more than one chosen from starch, sawdust, rice hull, corn stalk besides absorbent minerals. The chems. which can be absorbed and transferred to each organs of plants are chosen from glycine, glyphosate, hexazinone, imidachlopride, diazinone, or oxolinic acid. The prepn. can be directly inserted into the targeted harmful plants such as locust trees or arrowroots or in soil.				
IT	1071-83-6, Glyphosate RL: AGR (Agricultural use); BIOL (Biological study); USES (Uses) (agricultural chem. prepn. in pile type using absorbent minerals or natural org. matters as carrier)				
RN	1071-83-6 CAPLUS				
CN	Glycine, N-(phosphonomethyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)				



L73 ANSWER 2 OF 5 CAPLUS COPYRIGHT 2002 ACS
ACCESSION NUMBER: 2001:517625 CAPLUS
DOCUMENT NUMBER: 135:88635
TITLE: Agrochemical pesticide granules containing dextrin and
zeolite, and their manufacture
INVENTOR(S): Kawagishi, Akiyoshi
PATENT ASSIGNEE(S): Sankyo Co., Ltd., Japan
SOURCE: Jpn. Kokai Tokkyo Koho, 9 pp.

CODEN: JKXXAF
DOCUMENT TYPE: Patent
LANGUAGE: Japanese
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

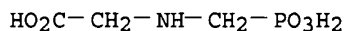
	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	JP 2001192302	A2	20010717	JP 2000-734	20000106
AB	The granules, which show low powder formation and good storage stability, are manufd. by granulation of compns. contg. active ingredients, dextrin, H2O and/or water-sol. org. solvents, and zeolites. Granules were prepd. from methomyl 80, Amycol No. 1 (dextrin) 8, H2O 2.5, ethylene glycol 2.5, and Sun-Zeolite 3S 7 wt. parts.				
IT	1071-83-6, Glyphosate RL: AGR (Agricultural use); BIOL (Biological study); USES (Uses) (agrochem. pesticide granules contg. dextrin and zeolite)				
RN	1071-83-6 CAPLUS				
CN	Glycine, N-(phosphonomethyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)				



L73 ANSWER 3 OF 5 CAPLUS COPYRIGHT 2002 ACS
ACCESSION NUMBER: 2001:78392 CAPLUS
DOCUMENT NUMBER: 134:116074
TITLE: Method of producing glyphosate or a salt thereof
INVENTOR(S): Muller, Ulrich; Merkle, Hans Rupert
PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
SOURCE: PCT Int. Appl., 25 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	WO 2001007447	A1	20010201	WO 2000-EP7003	20000721
	W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
	RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
	BR 2000012653	A	20020409	BR 2000-12653	20000721
	EP 1198466	A1	20020424	EP 2000-956244	20000721
	R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL				
PRIORITY APPLN. INFO.: DE 1999-19934599 A 19990723 WO 2000-EP7003 W 20000721					
AB	The invention relates to a method of producing N-phosphonomethylglycine or a salt thereof by contacting phosphonomethyliminodiacetic acid or a salt thereof with at least one oxygenous oxidant in the presence of a heterogeneous catalyst, said catalyst contg. at least one silicate.				
IT	1071-83-6P, N-Phosphonomethylglycine RL: SPN (Synthetic preparation); PREP (Preparation) (prepn. of)				
RN	1071-83-6 CAPLUS				

CN Glycine, N-(phosphonomethyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)



REFERENCE COUNT: 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L73 ANSWER 4 OF 5 CAPLUS COPYRIGHT 2002 ACS

ACCESSION NUMBER: 1995:441267 CAPLUS

DOCUMENT NUMBER: 122:186448

TITLE: Magnetized compound fertilizer and production method thereof

INVENTOR(S): Peng, Sigan; Li, Fangyi

PATENT ASSIGNEE(S): Sanyi Magnetic Fertilizer Technology Development Co., Ltd., Peop. Rep. China

SOURCE: Faming Zhuanli Shenqing Gongkai Shuomingshu, 9 pp.

CODEN: CNXXEV

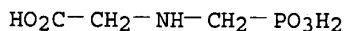
DOCUMENT TYPE: Patent

LANGUAGE: Chinese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	CN 1093695	A	19941019	CN 1994-104937	19940510
AB	The magnetized compd. fertilizer is prepd. from powd. coal ash, nitrogen fertilizer, phosphorus fertilizer, potassium fertilizer, zinc sulfate, borax, ammonium molybdate, copper sulfate, manganese sulfate, herbicides such as butachlor, insecticides such as DCIP.				
IT	1071-83-6, Glyphosate RL: AGR (Agricultural use); BIOL (Biological study); USES (Uses) (magnetized compd. fertilizer and prodn. method thereof)				
RN	1071-83-6 CAPLUS				
CN	Glycine, N-(phosphonomethyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)				



L73 ANSWER 5 OF 5 CAPLUS COPYRIGHT 2002 ACS

ACCESSION NUMBER: 1986:497686 CAPLUS

DOCUMENT NUMBER: 105:97686

TITLE: Oxidation with encapsulated cocatalyst

INVENTOR(S): Felthouse, Timothy R.

PATENT ASSIGNEE(S): Monsanto Co., USA

SOURCE: U.S., 9 pp.

CODEN: USXXAM

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
	US 4582650	A	19860415	US 1985-700170	19850211
OTHER SOURCE(S):	CASREACT 105:97686				
AB	HCHO, a reactive byproduct in the oxidative cleavage of (HO)2P(O)CH2N(CH2CO2H)2 (I) to (HO)2P(O)CH2NHCH2CO2H (II) using an activated carbon catalyst, is further oxidized to CO2 and H2O in the presence of a modified zeolite co-catalyst contg. an encapsulated noble metal at 75-150.degree. and 100-750 kPa. Thus, 4 g I,				

1 g Norit A activated carbon, and 0.15 g Pt encapsulated mordenite with pore openings < 8 .ANG., were treated with O at 95.degree. and atm. pressure to give 95% II.. The prepn. and modification of the catalysts are also described.

IT 1071-83-6P

RL: SPN (Synthetic preparation); PREP (Preparation)

(prepn. of, by oxidn. of phosphonomethyliminodiacetic acid using a zeoliteco-catalyst for concurrent oxidn. of formaldehyde)

RN 1071-83-6 CAPLUS

CN Glycine, N-(phosphonomethyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)



=> FIL CASREACT

COST IN U.S. DOLLARS	SINCE FILE	TOTAL
	ENTRY	SESSION
FULL ESTIMATED COST	34.74	531.84
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
	ENTRY	SESSION
CA SUBSCRIBER PRICE	-3.72	-27.89

FILE 'CASREACT' ENTERED AT 09:02:07 ON 13 DEC 2002
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FILE CONTENT:1907 - 8 Dec 2002 VOL 137 ISS 23

Some records from 1974 to 1991 are derived from the ZIC/VINITI data file and provided by InfoChem and some records are produced using some INPI data from the period prior to 1986.

This file contains CAS Registry Numbers for easy and accurate substance identification.

Crossover limits have been increased. See HELP RNCROSSOVER for details.

Structure search limits have been raised. See HELP SLIMIT for the new, higher limits.

=> D ACC 105:97686 ALL

ANSWER 1 CASREACT COPYRIGHT 2002 ACS

AN 105:97686 CASREACT

TI Oxidation with encapsulated cocatalyst

IN Felthouse, Timothy R.

PA Monsanto Co. , USA

SO U.S., 9 pp.

CODEN: USXXAM

DT Patent

LA English

IC ICM C07F009-38

NCL 260502500F

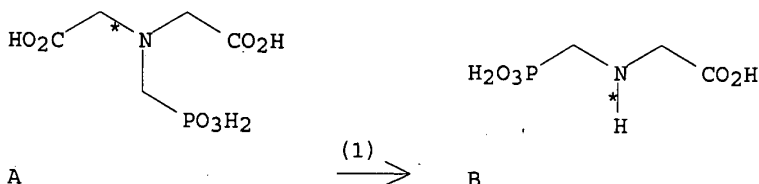
CC 29-7 (Organometallic and Organometalloidal Compounds)

Section cross-reference(s): 67

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 4582650	A	19860415	US 1985-700170	19850211
AB	HCHO, a reactive byproduct in the oxidative cleavage of (HO)2P(O)CH2N(CH2CO2H)2 (I) to (HO)2P(O)CH2NHCH2CO2H (II) using an activated carbon catalyst, is further oxidized to CO2 and H2O in the presence of a modified zeolite co-catalyst contg. an encapsulated noble metal at 75-150.degree. and 100-750 kPa. Thus, 4 g I, 1 g Norit A activated carbon, and 0.15 g Pt encapsulated mordenite with pore openings < 8 .ANG., were treated with O at 95.degree. and atm. pressure to give 95% II. The prepn. and modification of the catalysts are also described.				
ST	zeolite platinum encapsulated catalyst oxidn; phosphonomethylglycine; formaldehyde oxidn platinum encapsulated zeolite; phosphonomethyliminodiacetic acid oxidn zeolite catalyst				
IT	Oxidation catalysts (zeolites contg. encapsulated platinum, for formaldehyde and phosphonomethyliminodiacetic acid)				
IT	Zeolites, uses and miscellaneous RL: USES (Uses) (H mordenite-type, catalysts contg. encapsulated platinum and, for oxidn. of formaldehyde and phosphonomethyliminodiacetic acid)				
IT	Siloxanes and Silicones, uses and miscellaneous RL: USES (Uses) (di-Me, chlorine-terminated, for zeolite catalysts contg. encapsulated platinum)				
IT	7440-44-0, uses and miscellaneous RL: USES (Uses) (activated, catalyst, for oxidn. of phosphonomethyliminodiacetic acid)				
IT	7440-06-4, uses and miscellaneous RL: CAT (Catalyst use); USES (Uses) (catalysts, encapsulated in H-mordenite zeolite, for oxidn. of formaldehyde and phoosphonomethyliminodiacetic acid)				
IT	5994-61-6 RL: RCT (Reactant); RACT (Reactant or reagent) (oxidn. of, by activated carbon and zeoltite co-catalyst)				
IT	50-00-0, reactions RL: RCT (Reactant); RACT (Reactant or reagent) (oxidn. of, by platinum encapsulated zeolite)				
IT	1071-83-6P RL: SPN (Synthetic preparation); PREP (Preparation) (prepn. of, by oxidn. of phosphonomethyliminodiacetic acid using a zeoliteco-catalyst for concurrent oxidn. of formaldehyde)				

RX(1) OF 1 A ==> B

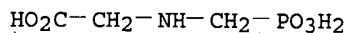


RX(1) RCT A 5994-61-6
PRO B 1071-83-6

=> s phosphonomethylglycine/cn
L2 1 PHOSPHONOMETHYLGLYCINE/CN

=> d

L2 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2002 ACS
RN 1071-83-6 REGISTRY
CN Glycine, N-(phosphonomethyl)-. (7CI, 8CI, 9CI) (CA INDEX NAME)
OTHER NAMES:
CN (Carboxymethylamino)methylphosphonic acid
CN Accord
CN Carboxymethylaminomethanephosphinic acid
CN Folusen
CN Forsat
CN Glialka
CN Glialka 36
CN Glyphodin A
CN Glyphosate
CN Glyphosate CT
CN Herbatop
CN Hockey
CN Lancer
CN MON 2139
CN MON 6000
CN N-Phosphomethylglycine
CN N-Phosphonomethylglycine
CN Phorsat
CN **Phosphonomethylglycine**
CN Phosphonomethyliminoacetic acid
CN Rebel Garden
FS 3D CONCORD
DR 37337-60-3, 75241-08-6, 42618-09-7
MF C3 H8 N O5 P
CI COM
LC STN Files: AGRICOLA, ANABSTR, AQUIRE, BEILSTEIN*, BIOBUSINESS, BIOSIS,
BIOTECHNO, CA, CABA, CANCERLIT, CAOLD, CAPLUS, CASREACT, CBNB, CEN,
CHEMCATS, CHEMINFORMRX, CHEMLIST, CIN, CSCHEM, CSNB, DDFU, DRUGU,
EMBASE, GMELIN*, HSDB*, IFICDB, IFIPAT, IFIUDB, IPA, MEDLINE, MRCK*,
MSDS-OHS, NIOSHTIC, PIRA, PROMT, RTECS*, SPECINFO, TOXCENTER, ULIDAT,
USPAT2, USPATFULL
(*File contains numerically searchable property data)
Other Sources: DSL**, EINECS**
(**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

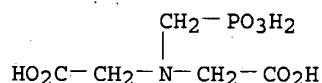
4269 REFERENCES IN FILE CA (1962 TO DATE)
245 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
4275 REFERENCES IN FILE CAPLUS (1962 TO DATE)
2 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

=> s phosphonomethyliminodiacetic acid/cn
L3 1 PHOSPHONOMETHYLIMINODIACETIC ACID/CN

=> d

L3 ANSWER 1 OF 1 REGISTRY COPYRIGHT 2002 ACS

RN 5994-61-6 REGISTRY
 CN Glycine, N-(carboxymethyl)-N-(phosphonomethyl)- (9CI) (CA INDEX NAME)
 OTHER CA INDEX NAMES:
 CN Acetic acid, [(phosphonomethyl)imino]di- (6CI, 7CI, 8CI)
 CN Phosphonic acid, [[bis(carboxymethyl)amino]methyl]-
 OTHER NAMES:
 CN Aminomethylphosphonic N,N-diacetic acid
 CN MON 820
 CN N-(Phosphonomethyl)iminodiacetic acid
 CN Nitrilodiacetic acid methylphosphonic acid
 CN **Phosphonomethyliminodiacetic acid**
 FS 3D CONCORD
 DR 178560-74-2
 MF C5 H10 N O7 P
 CI COM
 LC STN Files: BEILSTEIN*, BIOSIS, CA, CAOLD, CAPLUS, CASREACT, CHEMCATS,
 CHEMLIST, CSCHM, IFICDB, IFIPAT, IFIUDB, TOXCENTER, USPATFULL
 (*File contains numerically searchable property data)
 Other Sources: EINECS**
 (**Enter CHEMLIST File for up-to-date regulatory information)



PROPERTY DATA AVAILABLE IN THE 'PROP' FORMAT

212 REFERENCES IN FILE CA (1962 TO DATE)
 32 REFERENCES TO NON-SPECIFIC DERIVATIVES IN FILE CA
 215 REFERENCES IN FILE CAPLUS (1962 TO DATE)
 3 REFERENCES IN FILE CAOLD (PRIOR TO 1967)

=> file reg

COST IN U.S. DOLLARS

SINCE FILE	TOTAL
ENTRY	SESSION
15.54	15.75

FULL ESTIMATED COST

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STRUCTURE FILE UPDATES: 11 DEC 2002 HIGHEST RN 475975-25-8
 DICTIONARY FILE UPDATES: 11 DEC 2002 HIGHEST RN 475975-25-8

TSCA INFORMATION NOW CURRENT THROUGH MAY 20, 2002

Please note that search-term pricing does apply when conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP PROPERTIES for more information. See STN Note 27, Searching Properties in the CAS Registry File, for complete details:
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

```
=> s l1/prep and l2/rct
'PREP' IS NOT A VALID FIELD CODE
      0 PHOSPHONOMETHYLGLYCINE/PREP
      1 PHOSPHONOMETHYLGLYCINE/CN
L4      0 (PHOSPHONOMETHYLGLYCINE/PREP) AND (PHOSPHONOMETHYLGLYCINE/CN)
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=> file caplus
COST IN U.S. DOLLARS                SINCE FILE      TOTAL
                                     ENTRY      SESSION
FULL ESTIMATED COST                4.38        20.13
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FILE 'CAPLUS' ENTERED AT 06:57:54 ON 13 DEC 2002
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FILE COVERS 1907 - 13 Dec 2002 VOL 137 ISS 25
 FILE LAST UPDATED: 12 Dec 2002 (20021212/ED)

This file contains CAS Registry Numbers for easy and accurate substance identification.

CAS roles have been modified effective December 16, 2001. Please check your SDI profiles to see if they need to be revised. For information on CAS roles, enter HELP ROLES at an arrow prompt or use the CAS Roles thesaurus (/RL field) in this file.

```
=> s l1/prep and l2/rct
      4382 L1
      2944155 PREP/RL
      336 L1/PREP
          (L1 (L) PREP/RL)
      4275 L2
      2478124 RCT/RL
      136 L2/RCT
          (L2 (L) RCT/RL)
L5      34 L1/PREP AND L2/RCT

=> s l5 and (silicate or zeolite or clay or clathrasil)
      155779 SILICATE
      51696 SILICATES
      180610 SILICATE
          (SILICATE OR SILICATES)
      78216 ZEOLITE
      78017 ZEOLITES
      94194 ZEOLITE
          (ZEOLITE OR ZEOLITES)
      130301 CLAY
      58903 CLAYS
      148244 CLAY
          (CLAY OR CLAYS)
      66 CLATHRASIL
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51 CLATHRASILS
 92 CLATHRASIL
 (CLATHRASIL OR CLATHRASILS)
 L6 0 L5 AND (SILICATE OR ZEOLITE OR CLAY OR CLATHRASIL)

=> s 15 and heterogeneous catalyst
 95338 HETEROGENEOUS
 607972 CATALYST
 591842 CATALYSTS
 775424 CATALYST
 (CATALYST OR CATALYSTS)
 3961 HETEROGENEOUS CATALYST
 (HETEROGENEOUS (W) CATALYST)
 L7 0 L5 AND HETEROGENEOUS CATALYST

=> s 15 and catalyst
 607972 CATALYST
 591842 CATALYSTS
 775424 CATALYST
 (CATALYST OR CATALYSTS)
 L8 1 L5 AND CATALYST

=> d

L8 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2002 ACS
 AN 1999:529154 CAPLUS
 DN 131:144714
 TI Process for preparation of glyphosate by oxidizing N-substituted
 glyphosates
 IN Morgenstern, David A.; Fobian, Yvette M.
 PA Monsanto Company, USA
 SO PCT Int. Appl., 55 pp.
 CODEN: PIXXD2
 DT Patent
 LA English
 FAN.CNT 4

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI WO 9941260	A1	19990819	WO 1998-US2883	19980212
W: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, SD, SZ, UG, ZW, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG				
AU 9861663	A1	19990830	AU 1998-61663	19980212
AU 719152	B2	20000504		
US 6005140	A	19991221	US 1998-23404	19980212
EP 1062221	A1	20001227	EP 1998-906441	19980212
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, FI				
JP 2002510305	T2	20020402	JP 1999-503388	19980212
RU 2184118	C2	20020627	RU 1999-109599	19980212
ZA 9801219	A	19981124	ZA 1998-1219	19980213
TW 464537	B	20011121	TW 1998-87102054	19980213
US 6232494	B1	20010515	US 1999-263171	19990305
NO 9902246	A	19991011	NO 1999-2246	19990507
BR 9806202	A	20000215	BR 1998-6202	19990507
AU 728830	B2	20010118	AU 2000-17567	20000217
US 2001018536	A1	20010830	US 2001-776801	20010205
PRAI AU 1998-61663	A	19980212		
US 1998-22967	A	19980212		

US 1998-23404 A2 19980212
 WO 1998-US2883 A 19980212
 US 1998-96207P P 19980812
 US 1999-263171 A3 19990305
 OS CASREACT 131:144714; MARPAT 131:144714
 RE.CNT 7 THERE ARE 7 CITED REFERENCES AVAILABLE FOR THIS RECORD
 ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> d abs

L8 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2002 ACS
 AB This invention is directed to process for prepn. of
 $R3OC(O)CH_2NHCH_2P(O)(OR_4)(OR_5)$ (R_3, R_4, R_5 = independently H, substituted
 or unsubstituted hydrocarbyl, or an agronomically acceptable cation). The
 process comprises contacting a soln. with a noble metal **catalyst**
 and introducing oxygen into the soln. The soln. contains an N-substituted
 glyphosate $R3OC(O)CH_2N(CHR_1R_2)CH_2P(O)(OR_4)(OR_5)$ (R_1, R_2 = independently H,
 halo, $-PO_3H_2$, $-SO_3H_2$, $-NO_2$, (un)substituted hydrocarbyl other than $-CO_2H$).
 This invention also relates to an oxidn. **catalyst** comprising a
 noble metal having a hydrophobic electroactive mol. species adsorbed
 thereon. Thus, reaction of sarcosine with phosphorus acid in HCl followed
 by treatment with formalin gave 70.5% N-methylglyphosate. Platinum
 catalyzed oxidative dealkylation of N-methylglyphosate in water in the
 presence of oxygen gave 85.4% glyphosate.

=> file reg

COST IN U.S. DOLLARS	SINCE FILE	TOTAL
	ENTRY	SESSION
FULL ESTIMATED COST	18.12	38.25
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
	ENTRY	SESSION
CA SUBSCRIBER PRICE	-0.62	-0.62

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STRUCTURE FILE UPDATES: 12 DEC 2002 HIGHEST RN 476148-76-2
 DICTIONARY FILE UPDATES: 12 DEC 2002 HIGHEST RN 476148-76-2

TSCA INFORMATION NOW CURRENT THROUGH MAY 20, 2002

Please note that search-term pricing does apply when
 conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP
 PROPERTIES for more information. See STNote 27, Searching Properties
 in the CAS Registry File, for complete details:
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

=> s abw

L9 4 ABW

=> d scan

L9 4 ANSWERS REGISTRY COPYRIGHT 2002 ACS
IN DNA (mouse strain C57BL/6J clone UI-M-AL0-abw-d-07-0-UI EST
(expressed sequence tag) cDNA) (9CI)
SQL 357
MF Unspecified
CI MAN

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***
*** USE 'SQD' OR 'SQIDE' FORMATS TO DISPLAY SEQUENCE ***

HOW MANY MORE ANSWERS DO YOU WISH TO SCAN? (1):10

L9 4 ANSWERS REGISTRY COPYRIGHT 2002 ACS
IN DNA (mouse strain C57BL/6J clone UI-M-AL0-abw-e-06-0-UI EST
(expressed sequence tag)) (9CI)
SQL 451
MF Unspecified
CI MAN

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***
*** USE 'SQD' OR 'SQIDE' FORMATS TO DISPLAY SEQUENCE ***

L9 4 ANSWERS REGISTRY COPYRIGHT 2002 ACS
IN Uvitex ABW (9CI)
MF Unspecified
CI MAN

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

L9 4 ANSWERS REGISTRY COPYRIGHT 2002 ACS
IN Iron alloy, base, Fe,C,Cr,Mn,Mo,Si (ABW) (9CI)
MF C . Cr . Fe . Mn . Mo . Si
CI AYS

Component	Component Percent
Fe	89
Cr	6.5
C	2.1
Mn	1.1
Si	0.8
Mo	0.4

ALL ANSWERS HAVE BEEN SCANNED

16 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2002 ACS
AN 1983:144250 CAPLUS
DN 98:144250
TI Anion exchangers with imidazole groups
AU Veselova, L. P.; Nasakina, L. I.; Malakhova, E. V.
CS USSR
SO Deposited Doc. (1982), SPSTL 113 Khp-D82, 6 pp. Avail.: SPSTL
DT Report
LA Russian

=> d ibib abs

L16 ANSWER 1 OF 1 CAPLUS COPYRIGHT 2002 ACS
ACCESSION NUMBER: 1983:144250 CAPLUS
DOCUMENT NUMBER: 98:144250
TITLE: Anion exchangers with imidazole groups
AUTHOR(S): Veselova, L. P.; Nasakina, L. I.; Malakhova, E. V.
CORPORATE SOURCE: USSR
SOURCE: Deposited Doc. (1982), SPSTL 113 Khp-D82, 6 pp.
Avail.: SPSTL
DOCUMENT TYPE: Report
LANGUAGE: Russian
AB AI [85205-10-3] And AEI [85205-07-8] anion exchangers were
prepd. from chloromethylated divinylbenzene-styrene copolymer by
modification with imidazole and N-ethylimidazole, resp. The conversion
degree of the copolymer was detd. from the N content. The presence of
imidazole rings in the copolymers was shown by IR spectroscopy, and the
content of quaternary ammonium compd. in AEI by potentiometric titrn. with
0.1 M NaCl. Anionic complexes of Cu, Ni, Co, and Zn from HCl solns. were
selectively sorbed by the Cl-form anion exchangers at different HCl
concns. The max. sorption capacity of AEI for Cu, Co, and Zn was 2.05,
2.5, and 4.22 mequiv/g, resp., from 6, 10, and 3N HCl, resp. The sorption
capacity for Cu and Ni from weakly acidic solns. can be increased by
complexing with CNS-.

=> s aco/cn

REGISTRY INITIATED

Substance data SEARCH and crossover from CAS REGISTRY in progress...
Use DISPLAY HITSTR (or FHITSTR) to directly view retrieved structures.

L18 0 L17

=> file reg

COST IN U.S. DOLLARS	SINCE FILE	TOTAL
	ENTRY	SESSION
FULL ESTIMATED COST	0.40	113.29
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE	TOTAL
	ENTRY	SESSION
CA SUBSCRIBER PRICE	0.00	-1.24

FILE 'REGISTRY' ENTERED AT 07:04:15 ON 13 DEC 2002
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PLEASE SEE "HELP USAGETERMS" FOR DETAILS.
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Property values tagged with IC are from the ZIC/VINITI data file

provided by InfoChem.

STRUCTURE FILE UPDATES: 12 DEC 2002 HIGHEST RN 476148-76-2
DICTIONARY FILE UPDATES: 12 DEC 2002 HIGHEST RN 476148-76-2

TSCA INFORMATION NOW CURRENT THROUGH MAY 20, 2002

Please note that search-term pricing does apply when
conducting SmartSELECT searches.

Crossover limits have been increased. See HELP CROSSOVER for details.

Experimental and calculated property data are now available. See HELP
PROPERTIES for more information. See STNote 27, Searching Properties
in the CAS Registry File, for complete details:
<http://www.cas.org/ONLINE/STN/STNOTES/stnotes27.pdf>

=> s aco/cn

L19 0 ACO/CN

=> s aen/cn

L20 0 AEN/CN

=> s aen

L21 12 AEN

=> d scan

L21 12 ANSWERS REGISTRY COPYRIGHT 2002 ACS
IN Cirrasol AEN-XB (9CI)
MF Unspecified
CI MAN

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

HOW MANY MORE ANSWERS DO YOU WISH TO SCAN? (1):10

L21 12 ANSWERS REGISTRY COPYRIGHT 2002 ACS
IN Cirrasol AEN-XF (9CI)
MF Unspecified
CI MAN

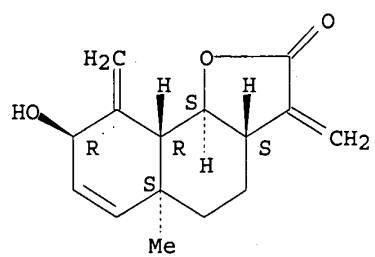
*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

L21 12 ANSWERS REGISTRY COPYRIGHT 2002 ACS
IN Cirrasol AEN-ZX (9CI)
MF Unspecified
CI MAN

*** STRUCTURE DIAGRAM IS NOT AVAILABLE ***

L21 12 ANSWERS REGISTRY COPYRIGHT 2002 ACS
IN Naphtho[1,2-b]furan-2(3H)-one, 3a,4,5,5a,8,9,9a,9b-octahydro-8-hydroxy-5a-
methyl-3,9-bis(methylene)-, (3aS,5aS,8R,9aR,9bS) - (9CI)
MF C15 H18 O3

Absolute stereochemistry.



=> s l2/prep and l3/rct
 4275 L2
 2944155 PREP/RL
 298 L2/PREP
 (L2 (L) .PREP/RL)
 214 L3
 2478124 RCT/RL
 77 L3/RCT
 (L3 (L) RCT/RL)
 L28 52 L2/PREP AND L3/RCT

=> s l28 and (silicate or zeolite or clay or clathrasil)
 155779 SILICATE
 51696 SILICATES
 180610 SILICATE
 (SILICATE OR SILICATES)
 78216 ZEOLITE
 78017 ZEOLITES
 94194 ZEOLITE
 (ZEOLITE OR ZEOLITES)
 130301 CLAY
 58903 CLAYS
 148244 CLAY
 (CLAY OR CLAYS)
 66 CLATHRASIL
 51 CLATHRASILS
 92 CLATHRASIL
 (CLATHRASIL OR CLATHRASILS)
 L29 2 L28 AND (SILICATE OR ZEOLITE OR CLAY OR CLATHRASIL)

=> d ibib abs hitstr

L29 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2002 ACS
 ACCESSION NUMBER: 2001:78392 CAPLUS
 DOCUMENT NUMBER: 134:116074
 TITLE: Method of producing glyphosate or a salt thereof
 INVENTOR(S): Muller, Ulrich; Merkle, Hans Rupert
 PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany
 SOURCE: PCT Int. Appl., 25 pp.
 CODEN: PIXXD2
 DOCUMENT TYPE: Patent
 LANGUAGE: German
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

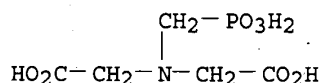
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001007447	A1	20010201	WO 2000-EP7003	20000721
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG				
BR 2000012653	A	20020409	BR 2000-12653	20000721
EP 1198466	A1	20020424	EP 2000-956244	20000721
R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL				
PRIORITY APPLN. INFO.:			DE 1999-19934599 A	19990723
			WO 2000-EP7003	W 20000721

AB The invention relates to a method of producing N-phosphonomethylglycine or a salt thereof by contacting phosphonomethyliminodiacetic acid or a salt thereof with at least one oxygenous oxidant in the presence of a heterogeneous catalyst, said catalyst contg. at least one silicate

IT 1071-83-6P, N-Phosphonomethylglycine
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)
RN 1071-83-6 CAPLUS
CN Glycine, N-(phosphonomethyl)-, (7CI, 8CI, 9CI) (CA INDEX NAME)



IT 5994-61-6, Phosphonomethyliminodiacetic acid
RL: RCT (Reactant); RACT (Reactant or reagent)
(silicate catalyzed oxidn. of)
RN 5994-61-6 CAPLUS
CN Glycine, N-(carboxymethyl)-N-(phosphonomethyl)- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 4 THERE ARE 4 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> d ibib abs hitstr 2

L29 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2002 ACS
ACCESSION NUMBER: 1986:497686 CAPLUS
DOCUMENT NUMBER: 105:97686
TITLE: Oxidation with encapsulated cocatalyst
INVENTOR(S): Felthouse, Timothy R.
PATENT ASSIGNEE(S): Monsanto Co., USA
SOURCE: U.S., 9 pp.
CODEN: USXXAM
DOCUMENT TYPE: Patent
LANGUAGE: English
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

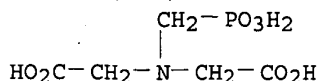
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 4582650	A	19860415	US 1985-700170	19850211

OTHER SOURCE(S): CASREACT 105:97686

AB HCHO, a reactive byproduct in the oxidative cleavage of (HO)2P(O)CH2N(CH2CO2H)2 (I) to (HO)2P(O)CH2NHCH2CO2H (II) using an activated carbon catalyst, is further oxidized to CO2 and H2O in the presence of a modified zeolite co-catalyst contg. an encapsulated noble metal at 75-150.degree. and 100-750 kPa. Thus, 4 g I, 1 g Norit A activated carbon, and 0.15 g Pt encapsulated mordenite with pore openings < 8 .ANG., were treated with O at 95.degree. and atm. pressure to give 95% II. The prepn. and modification of the catalysts are also described.

IT 5994-61-6
RL: RCT (Reactant); RACT (Reactant or reagent)
(oxidn. of, by activated carbon and zeolite co-catalyst)

RN 5994-61-6 CAPLUS
CN Glycine, N-(carboxymethyl)-N-(phosphonomethyl)- (9CI) (CA INDEX NAME)



IT 1071-83-6P
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of, by oxidn. of phosphonomethyliminodiacetic acid using a
zeoliteco-catalyst for concurrent oxidn. of formaldehyde)
RN 1071-83-6 CAPLUS
CN Glycine, N-(phosphonomethyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)



=> s 128 and heterogeneous catalyst
95338 HETEROGENEOUS
607972 CATALYST
591842 CATALYSTS
775424 CATALYST
(CATALYST OR CATALYSTS)
3961 HETEROGENEOUS CATALYST
(HETEROGENEOUS (W) CATALYST)
L30 3 L28 AND HETEROGENEOUS CATALYST

=> d ibib abs hitstr 1-3

L30 ANSWER 1 OF 3 CAPLUS COPYRIGHT 2002 ACS
ACCESSION NUMBER: 2001:618009 CAPLUS
DOCUMENT NUMBER: 135:180876
TITLE: Method for producing N-(phosphonomethyl)glycine
INVENTOR(S): Hitzler, Martin; Thalhammer, Franz; Hammer, Benedikt
PATENT ASSIGNEE(S): Skw Trostberg Aktiengesellschaft, Germany
SOURCE: PCT Int. Appl., 24 pp.
CODEN: PIXXD2
DOCUMENT TYPE: Patent
LANGUAGE: German
FAMILY ACC. NUM. COUNT: 1
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001060830	A1	20010823	WO 2001-EP1749	20010216
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM			
RW:	GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG			
DE 10007702	A1	20010823	DE 2000-10007702	20000219
EP 1257557	A1	20021120	EP 2001-936052	20010216
R:	AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,			

IE, SI, LT, LV, FI, RO, MK, CY, AL, TR
PRIORITY APPLN. INFO.: DE 2000-10007702 A 20000219
WO 2001-EP1749 W 20010216

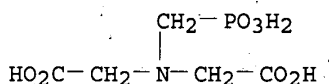
OTHER SOURCE(S): CASREACT 135:180876

AB The invention relates to a method for producing N-(phosphonomethyl)glycine involving the following steps: (a) oxidizing N-(phosphonomethyl)iminodiacetic acid (PMIDA) with peroxides or oxygen in an aq. medium and in the presence of a **heterogeneous catalyst** at a temp. ranging from 50 to 150.degree.; (b) subsequently sepg. the solid catalyst out of the aq. reaction suspension of step (a); (c) concg. the clear reaction soln. from step (b), esp. by evapn., and; (d) sepg. the N-(phosphonomethyl)glycine out of the concd. reaction soln. from step (c), esp. by filtration. According to the invention, the aq. reaction soln. from step (d) (mother liquor) is returned with small amts. of N-(phosphonomethyl)glycine and byproducts to step (b) (catalyst sepn.) and/or to step (c) (concn.). This results in distinctly increasing the yield with a const. product purity and in noticeably reducing the amt. of mother liquor.

IT 5994-61-6, N-(Phosphonomethyl)iminodiacetic acid
RL: RCT (Reactant); RACT (Reactant or reagent)
(heterogeneous catalyst mediated peroxide oxidn. of)

RN 5994-61-6 CAPLUS

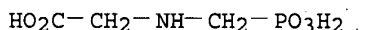
CN Glycine, N-(carboxymethyl)-N-(phosphonomethyl)- (9CI) (CA INDEX NAME)



IT 1071-83-6P, N-(Phosphonomethyl)glycine
RL: SPN (Synthetic preparation); PREP (Preparation)
(prepn. of)

RN 1071-83-6 CAPLUS

CN Glycine, N-(phosphonomethyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)



REFERENCE COUNT: 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L30 ANSWER 2 OF 3 CAPLUS COPYRIGHT 2002 ACS

ACCESSION NUMBER: 2001:136726 CAPLUS

DOCUMENT NUMBER: 134:163173

TITLE: Procedure for the production of N-(phosphonomethyl)glycine

INVENTOR(S): Hitzler, Martin; Fleischer, Frank; Hammer, Benedikt

PATENT ASSIGNEE(S): Skw Trostberg A.-G., Germany

SOURCE: Ger. Offen., 6 pp.

CODEN: GWXXBX

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
DE 19938622	A1	20010222	DE 1999-19938622	19990814
DE 19938622	C2	20021002		

OTHER SOURCE(S): CASREACT 134:163173

AB In a procedure for prodn. of N-(phosphonomethyl)glycine by oxidn. of N-(phosphonomethyl)iminodiacetic acid with peroxides in aq. medium in presence of a **heterogeneous catalyst** in the temp. range from 50 to 100.degree., the sepn. of product from catalyst in aq. reaction suspension is described. According to invention, the activated charcoal catalysts are used for high product selectivity with high const. activity and yield with continuous product purity.

IT **1071-83-6P**, N-(Phosphonomethyl)glycine
 RL: PUR (Purification or recovery); SPN (Synthetic preparation); **PREP** (Preparation)
 (procedure for sepn. of (phosphonomethyl)glycine from peroxides in **heterogeneous catalyst** mediated oxidn. of (phosphonomethyl)iminodiacetic acid)

RN 1071-83-6 CAPLUS

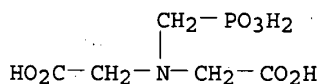
CN Glycine, N-(phosphonomethyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)



IT **5994-61-6**, N-(Phosphonomethyl)iminodiacetic acid
 RL: **RCT (Reactant)**; RACT (Reactant or reagent)
 (procedure for sepn. of (phosphonomethyl)glycine from peroxides in **heterogeneous catalyst** mediated oxidn. of (phosphonomethyl)iminodiacetic acid)

RN 5994-61-6 CAPLUS

CN Glycine, N-(carboxymethyl)-N-(phosphonomethyl)- (9CI) (CA INDEX NAME)



REFERENCE COUNT: 3 THERE ARE 3 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L30 ANSWER 3 OF 3 CAPLUS COPYRIGHT 2002 ACS

ACCESSION NUMBER: 2001:78392 CAPLUS

DOCUMENT NUMBER: 134:116074

TITLE: Method of producing glyphosate or a salt thereof

INVENTOR(S): Muller, Ulrich; Merkle, Hans Rupert

PATENT ASSIGNEE(S): BASF Aktiengesellschaft, Germany

SOURCE: PCT Int. Appl., 25 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2001007447	A1	20010201	WO 2000-EP7003	20000721
W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM				
RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ,				

CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG
 BR 2000012653 A 20020409 BR 2000-12653 20000721
 EP 1198466 A1 20020424 EP 2000-956244 20000721

R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT,
 IE, SI, LT, LV, FI, RO, MK, CY, AL

PRIORITY APPLN. INFO.:

DE 1999-19934599 A 19990723
 WO 2000-EP7003 W 20000721

AB The invention relates to a method of producing N-phosphonomethylglycine or a salt thereof by contacting phosphonomethyliminodiacetic acid or a salt thereof with at least one oxygenous oxidant in the presence of a heterogeneous catalyst, said catalyst contg. at least one silicate.

IT 1071-83-6P, N-Phosphonomethylglycine
 RL: SPN (Synthetic preparation); PREP (Preparation)
 (prepn. of)

RN 1071-83-6 CAPLUS

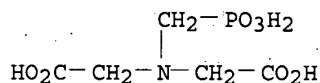
CN Glycine, N-(phosphonomethyl)- (7CI, 8CI, 9CI) (CA INDEX NAME)



IT 5994-61-6, Phosphonomethyliminodiacetic acid
 RL: RCT (Reactant); RACT (Reactant or reagent)
 (silicate catalyzed oxidn. of)

RN 5994-61-6 CAPLUS

CN Glycine, N-(carboxymethyl)-N-(phosphonomethyl)- (9CI) (CA INDEX NAME)



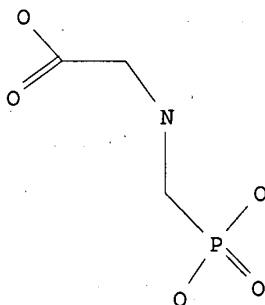
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L31 1 L2

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L31 ANSWER 1 OF 1 BEILSTEIN COPYRIGHT 2002 BEILSTEIN CDS MDL

Beilstein Records (BRN): 2045054
Beilstein Pref. RN (BPR): 1071-83-6
CAS Reg. No. (RN): 1071-83-6
Chemical Name (CN): Carboxymethylamino-methylphosphonic acid,
N-phosphonomethylglycine, glyphosate
Autonom Name (AUN): (phosphonomethyl-amino)-acetic acid
Molec. Formula (MF): C3 H8 N O5 P
Molecular Weight (MW): 169.07
Lawson Number (LN): 3379, 689
Compound Type (CTYPE): acyclic
Constitution ID (CONSID): 1869193
Tautomer ID (TAUTID): 1975577
Beilstein Citation (BSO): 5-04, 6-04
Entry Date (DED): 1989/06/29
Update Date (DUPD): 2002/01/24



Field Availability:

Code	Name	Occurrence
BRN	Beilstein Records	1
BPR	Beilstein Preferred RN	1
RN	CAS Registry Number	1
CN	Chemical Name	3
AUN	Autonomname	1
MF	Molecular Formula	1
FW	Formular Weight	1
LN	Lawson Number	2
CTYPE	Compound Type	1
CONSID	Constitution ID	1
TAUTID	Tautomer ID	1
BSO	Beilstein Citation	2
ED	Entry Date	1
UPD	Update Date	1
ADSM	Adsorption (MCS)	3
ASSM	Association (MCS)	33
BIO	Biological Behaviour	2
BIOD	Biodegradation	9

CDEN	Density (Crystal)	4
CDER	Chemical Derivative	4
CNF	Conformation	1
COEV	Concentration in Environment	8
CRYPH	Crystal Phase	6
CSG	Crystal Space Group	3
CSYS	Crystal System	1
DE	Dissociation Exponent	17
ECS	Stability in Soil	2
ECTD	Ecological Mobility	9
ECTOX	Ecotoxicology	76
ELCB	Electrochemical Behaviour	3
EXCA	Exposure Assessment	1
FINFO	Further Information	1
GEO	Interatomic Distance and Angle	1
IR	Infrared Spectrum	7
LLSM	Liquid/Liquid System (MCS)	1
MP	Melting Point	7
MS	Mass Spectrum	1
NMR	Nuclear Magnetic Resonance	30
PHARM	Pharmacological Data	25
SLB	Solubility (MCS)	2
USC	Use of Compound	8
XREF	Crossfile Reference	6

This substance also occurs in Reaction Documents:

Code	Name	Occurrence
=====		
RX	Reaction Documents	49
RXREA	Substance is Reaction Reactant	7
RXPRO	Substance is Reaction Product	42

=> d frxpro

L31 ANSWER 1 OF 1 BEILSTEIN COPYRIGHT 2002 BEILSTEIN CDS MDL

Reaction:

RX

Reaction ID (.ID): 7249400
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 7249400.1
Reaction Classification (.CL): Preparation (half reaction)
Reference(s):
1. Patent: Budapesti Vegyimuvek FR 2276312 1976, Chem.Abstr., 85(21610)
2. Patent: Monsanto Co. US 3927080 1975, Chem.Abstr., 84(105763)
3. Patent: Monsanto Co. DE 2152826 1972, Chem.Abstr., 77(165079)
4. Patent: ICI DE 2355351 1974, Chem.Abstr., 81(91931)

Reaction:

RX

Reaction ID (.ID): 5142663
Reactant BRN (.RBRN): 1795744
Reactant (.RCT): phosphonomethylimino-di-acetic acid
Product BRN (.PBRN): 2045054, 1701219
Product (.PRO): Carboxymethylamino-methylphosphonic acid,
aminomethyl-phosphonic acid

No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 5142663.1
Reaction Classification (.CL): Chemical behaviour
Reagent (.RGT): air, active carbon 4S
Temperature (.T): 95 Cel
Other Conditions (.COND): other carbon catalysts
Reference(s):
1. Pinel, Catherine; Landrison, Emmanuel; Lini, Hedi; Gallezot, Pierre,
J.Catal., CODEN: JCTLA5, 182(2), <1999>, 515 - 519; BABS-6171630

Reaction:

RX

Reaction ID (.ID): 4906248
Reactant BRN (.RBRN): 7942758
Reactant (.RCT): (5-oxo-2,2-bis-trifluoromethyl-oxazolidin-3-ylmethyl)-phosphonic acid dimethyl ester
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 4906248.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): 1.) hydrochloric acid, 2.) propene oxide
Other Conditions (.COND): 1.) reflux, 2.) EtOH
Note(s) (.COM): Yield given. Multistep reaction
Reference(s):
1. Spengler, Jan; Burger, Klaus, J.Chem.Soc.Perkin Trans.1, CODEN:
JCPRB4(13), <1998>, 2091-2096; BABS-6095628

Reaction:

RX

Reaction ID (.ID): 4861100
Reactant BRN (.RBRN): 1701219, 1209322
Reactant (.RCT): aminomethyl-phosphonic acid, hydroxyacetic acid
Product BRN (.PBRN): 2045054, 1209246, 741891, 385686
Product (.PRO): Carboxymethylamino-methylphosphonic acid, formic acid, oxoacetic acid, oxalic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 4861100.1
Reaction Classification (.CL): Chemical behaviour
Reagent (.RGT): 1) A. niger catalase, spinach glycolate oxidase, flavine mononucleotide, AMPA, O2, 2.) H2
Catalyst (.CAT): 2.) Pd/C
Other Conditions (.COND): multistep reaction; other reagents, buffers, pressure; reaction time and concentration dependences
Subject Studied (.SUBJ): Product distribution
Reference(s):
1. Gavagan, John E.; Fager, Susan K.; Seip, John E.; Clark, Dawn S.; Payne, Mark S.; et al., J.Org.Chem., CODEN: JOCEAH, 62(16), <1997>, 5419-5427; BABS-6088916

Reaction:

RX

Reaction ID (.ID): 4861099
Reactant BRN (.RBRN): 1209322, 1701219
Reactant (.RCT): hydroxyacetic acid, aminomethyl-phosphonic acid
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 4861099.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): 1.) O₂, spinach glycolate oxidase, A niger catalase, FMN, butyric acid

Reference(s):

1. Gavagan, John E.; Fager, Susan K.; Seip, John E.; Clark, Dawn S.; Payne, Mark S.; et al., J.Org.Chem., CODEN: JOCEAH, 62(16), <1997>, 5419-5427; BABS-6088916

Reaction:

RX

Reaction ID (.ID): 3726364
Reactant BRN (.RBRN): 6992960
Reactant (.RCT): C11H23NO5P(1-)*K(1+)
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3726364.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): HCl conc
Solvent (.SOL): H₂O
Time (.TIM): 4 hour(s)
Other Conditions (.COND): Heating
Note(s) (.COM): Yield given

Reference(s):

1. Golovanov, A. V.; Maslennikov, I. G.; Ladygina, M. G.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 85-87, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(1), <1987>, 101-103; BABS-5911326

Reaction:

RX

Reaction ID (.ID): 3702281
Reactant BRN (.RBRN): 6885729
Reactant (.RCT): C19H39NO5P(1-)*Na(1+)
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3702281.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): conc. HCl
Solvent (.SOL): H₂O
Time (.TIM): 4 hour(s)
Temperature (.T): 100 Cel
Note(s) (.COM): Yield given

Reference(s):

1. Golovanov, A. V.; Maslennikov, I. G.; Medvedev, A. E.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 56, <1986>, 1791-1793, Zh.Obshch.Khim., CODEN: ZOKHA4, 56(9), <1986>, 2031-2034;

BABS-5874571

Reaction:

RX

Reaction ID (.ID): 3702214
Reactant BRN (.RBRN): 6885448
Reactant (.RCT): C17H35NO5P(1-)*Na(1+)
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3702214.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): conc. HCl
Solvent (.SOL): H2O
Time (.TIM): 4 hour(s)
Temperature (.T): 100 Cel
Note(s) (.COM): Yield given
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Medvedev, A. E.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 56, <1986>, 1791-1793, Zh.Obshch.Khim., CODEN: ZOKHA4, 56(9), <1986>, 2031-2034; BABS-5874571

Reaction:

RX

Reaction ID (.ID): 3702101
Reactant BRN (.RBRN): 6885010
Reactant (.RCT): C15H31NO5P(1-)*Na(1+)
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3702101.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): conc. HCl
Solvent (.SOL): H2O
Time (.TIM): 4 hour(s)
Temperature (.T): 100 Cel
Note(s) (.COM): Yield given
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Medvedev, A. E.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 56, <1986>, 1791-1793, Zh.Obshch.Khim., CODEN: ZOKHA4, 56(9), <1986>, 2031-2034; BABS-5874571

Reaction:

RX

Reaction ID (.ID): 3702037
Reactant BRN (.RBRN): 6884719
Reactant (.RCT): C13H27NO5P(1-)*Na(1+)
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3702037.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): conc. HCl

Solvent (.SOL): H2O
Time (.TIM): 4 hour(s)
Temperature (.T): 100 Cel
Note(s) (.COM): Yield given
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Medvedev, A. E.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 56, <1986>, 1791-1793, Zh.Obshch.Khim., CODEN: ZOKHA4, 56(9), <1986>, 2031-2034; BABS-5874571

Reaction:

RX

Reaction ID (.ID): 3701940
Reactant BRN (.RBRN): 6884314
Reactant (.RCT): C11H23NO5P(1-)*Na(1+)
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 2

Reaction Details:

RX

Reaction RID (.RID): 3701940.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): conc. HCl
Solvent (.SOL): H2O
Time (.TIM): 4 hour(s)
Temperature (.T): 100 Cel
Note(s) (.COM): Yield given
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Medvedev, A. E.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 56, <1986>, 1791-1793, Zh.Obshch.Khim., CODEN: ZOKHA4, 56(9), <1986>, 2031-2034; BABS-5874571

RX

Reaction RID (.RID): 3701940.2
Reaction Classification (.CL): Preparation
Reagent (.RGT): HCl conc.
Solvent (.SOL): H2O
Time (.TIM): 4 hour(s)
Other Conditions (.COND): Heating
Note(s) (.COM): Yield given
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Ladygina, M. G.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 85-87, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(1), <1987>, 101-103; BABS-5911326

Reaction:

RX

Reaction ID (.ID): 3701807
Reactant BRN (.RBRN): 6883849
Reactant (.RCT): C9H19NO5P(1-)*Na(1+)
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3701807.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): conc. HCl
Solvent (.SOL): H2O
Time (.TIM): 4 hour(s)
Temperature (.T): 100 Cel
Note(s) (.COM): Yield given

Reference(s):

1. Golovanov, A. V.; Maslennikov, I. G.; Medvedev, A. E.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 56, <1986>, 1791-1793, Zh.Obshch.Khim., CODEN: ZOKHA4, 56(9), <1986>, 2031-2034; BABS-5874571

Reaction:

RX

Reaction ID (.ID): 3701595
Reactant BRN (.RBRN): 6882989
Reactant (.RCT): C7H15NO5P(1-)*Na(1+)
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3701595.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): conc. HCl
Solvent (.SOL): H2O
Time (.TIM): 4 hour(s)
Temperature (.T): 100 Cel
Note(s) (.COM): Yield given
Reference(s):

1. Golovanov, A. V.; Maslennikov, I. G.; Medvedev, A. E.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 56, <1986>, 1791-1793, Zh.Obshch.Khim., CODEN: ZOKHA4, 56(9), <1986>, 2031-2034; BABS-5874571

Reaction:

RX

Reaction ID (.ID): 3701496
Reactant BRN (.RBRN): 6882542
Reactant (.RCT): C5H11NO5P(1-)*Na(1+)
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3701496.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): conc. HCl
Solvent (.SOL): H2O
Time (.TIM): 4 hour(s)
Temperature (.T): 100 Cel
Note(s) (.COM): Yield given
Reference(s):

1. Golovanov, A. V.; Maslennikov, I. G.; Medvedev, A. E.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 56, <1986>, 1791-1793, Zh.Obshch.Khim., CODEN: ZOKHA4, 56(9), <1986>, 2031-2034; BABS-5874571

Reaction:

RX

Reaction ID (.ID): 3571132
Reactant BRN (.RBRN): 6393519
Reactant (.RCT): trimethyl ester of
<<(carboxymethyl)amino>methyl>phosphonic acid
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 3

Reaction Details:

RX

Reaction RID (.RID): 3571132.1
Reaction Classification (.CL): Preparation
Yield (.YDT): 85 percent (BRN=2045054)
Reagent (.RGT): conc. HCl
Time (.TIM): 4 hour(s)
Other Conditions (.COND): Heating
Reference(s):
1. Barsukov, A. V.; Yaroshenko, G. F.; Lastovskii, R. P.; Dyatlova, N. M., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 53(6), <1983>, 1109-1114, Zh.Obshch.Khim., CODEN: ZOKHA4, 53(6), <1983>, 1243-1249; BABS-5802172

RX

Reaction RID (.RID): 3571132.2
Reaction Classification (.CL): Preparation
Reagent (.RGT): conc. hydrochloric acid
Time (.TIM): 4 hour(s)
Other Conditions (.COND): Heating
Note(s) (.COM): Yield given
Reference(s):
1. Barsukov, A. V.; Matkovskaya, T. A.; Yaroshenko, G. F.; Allakhverdiv, G. R.; Dyatlova, N. M., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 54, <1984>, 933-936, Zh.Obshch.Khim., CODEN: ZOKHA4, 54(5), <1984>, 1045-1048; BABS-5871201

RX

Reaction RID (.RID): 3571132.3
Reaction Classification (.CL): Preparation
Reagent (.RGT): conc. HCl, H2O
Time (.TIM): 6 hour(s)
Other Conditions (.COND): Heating
Note(s) (.COM): Yield given
Reference(s):
1. Barsukov, A. V.; Zhdanov, B. V.; Markovskaya, T. A.; Kaslina, N. A.; Polyakova, I. A.; et al., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 55(7), <1985>, 1417-1423, Zh.Obshch.Khim., CODEN: ZOKHA4, 55(7), <1985>, 1594-1600; BABS-5871372

Reaction:

RX

Reaction ID (.ID): 3538941
Reactant BRN (.RBRN): 635782, 6892122
Reactant (.RCT): glycine, chloromethyl-(1,1,2,2,2-pentafluoro-ethyl)-phosphinic acid propyl ester
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538941.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): 1.) 50percent NaOH
Other Conditions (.COND): 1.) water, 80-90 deg C, 2 h; 2.) reflux, 28 h
Note(s) (.COM): Multistep reaction
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538940
Reactant BRN (.RBRN): 635782, 6892122
Reactant (.RCT): glycine, chloromethyl-(1,1,2,2,2-pentafluoro-ethyl)-phosphinic acid propyl ester
Product BRN (.PBRN): 2045054, 1731035
Product (.PRO): Carboxymethylamino-methylphosphonic acid, trifluoromethane
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538940.1
Reaction Classification (.CL): Chemical behaviour
Reagent (.RGT): NaOH
Solvent (.SOL): ethanol, H2O
Temperature (.T): 20 Cel
Subject Studied (.SUBJ): Rate constant
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538939
Reactant BRN (.RBRN): 635782, 6891922
Reactant (.RCT): glycine, methyl (chloromethyl)(pentafluoroethyl)phosphinate
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538939.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): 1.) 50percent NaOH
Other Conditions (.COND): 1.) water, 80-90 deg C, 2 h; 2.) reflux, 28 h
Note(s) (.COM): Multistep reaction
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538938
Reactant BRN (.RBRN): 635782, 6891922
Reactant (.RCT): glycine, methyl (chloromethyl)(pentafluoroethyl)phosphinate
Product BRN (.PBRN): 2045054, 1731035
Product (.PRO): Carboxymethylamino-methylphosphonic acid, trifluoromethane
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538938.1
Reaction Classification (.CL): Chemical behaviour
Reagent (.RGT): NaOH
Solvent (.SOL): ethanol, H2O
Temperature (.T): 20 Cel
Subject Studied (.SUBJ): Rate constant
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538937
Reactant BRN (.RBRN): 635782, 6891912
Reactant (.RCT): glycine, chloromethyl-(1,1,2,2,2-pentafluoro-ethyl)-phosphinic acid ethyl ester
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538937.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): 1.) 50percent NaOH
Other Conditions (.COND): 1.) water, 80-90 deg C, 2 h; 2.) reflux, 28 h
Note(s) (.COM): Multistep reaction
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538936
Reactant BRN (.RBRN): 635782, 6891912
Reactant (.RCT): glycine, chloromethyl-(1,1,2,2,2-pentafluoro-ethyl)-phosphinic acid ethyl ester
Product BRN (.PBRN): 2045054, 1731035
Product (.PRO): Carboxymethylamino-methylphosphonic acid, trifluoromethane
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538936.1
Reaction Classification (.CL): Chemical behaviour
Reagent (.RGT): NaOH
Solvent (.SOL): ethanol, H2O
Temperature (.T): 20 Cel
Subject Studied (.SUBJ): Rate constant
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538935
 Reactant BRN (.RBRN): 635782, 6891670
 Reactant (.RCT): glycine, chloromethyl-trifluoromethyl-
 phosphinic acid hexyl ester
 Product BRN (.PBRN): 2045054
 Product (.PRO): Carboxymethylamino-methylphosphonic acid
 No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538935.1
 Reaction Classification (.CL): Preparation
 Reagent (.RGT): 1.) 50percent NaOH
 Other Conditions (.COND): 1.) water, 80-90 deg C, 2 h; 2.) reflux,
 28 h
 Note(s) (.COM): Multistep reaction
 Reference(s):
 1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L.
 N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4,
 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>,
 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538934
 Reactant BRN (.RBRN): 635782, 6891670
 Reactant (.RCT): glycine, chloromethyl-trifluoromethyl-
 phosphinic acid hexyl ester
 Product BRN (.PBRN): 2045054, 1731035
 Product (.PRO): Carboxymethylamino-methylphosphonic acid,
 trifluoromethane
 No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538934.1
 Reaction Classification (.CL): Chemical behaviour
 Reagent (.RGT): NaOH
 Solvent (.SOL): ethanol, H2O
 Temperature (.T): 20 Cel
 Subject Studied (.SUBJ): Rate constant
 Reference(s):
 1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L.
 N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4,
 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>,
 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538933
 Reactant BRN (.RBRN): 635782, 6891288
 Reactant (.RCT): glycine, chloromethyl-trifluoromethyl-
 phosphinic acid butyl ester
 Product BRN (.PBRN): 2045054
 Product (.PRO): Carboxymethylamino-methylphosphonic acid
 No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538933.1
 Reaction Classification (.CL): Preparation
 Reagent (.RGT): 1.) 50percent NaOH

Other Conditions (.COND): 1.) water, 80-90 deg C, 2 h; 2.) reflux, 28 h
Note(s) (.COM): Multistep reaction
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538932
Reactant BRN (.RBRN): 635782, 6891288
Reactant (.RCT): glycine, chloromethyl-trifluoromethyl-phosphinic acid butyl ester
Product BRN (.PBRN): 2045054, 1731035
Product (.PRO): Carboxymethylamino-methylphosphonic acid, trifluoromethane
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538932.1
Reaction Classification (.CL): Chemical behaviour
Reagent (.RGT): NaOH
Solvent (.SOL): ethanol, H2O
Temperature (.T): 20 Cel
Subject Studied (.SUBJ): Rate constant
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538931
Reactant BRN (.RBRN): 635782, 6891040
Reactant (.RCT): glycine, chloromethyl-trifluoromethyl-phosphinic acid propyl ester
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538931.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): 1.) 50percent NaOH
Other Conditions (.COND): 1.) water, 80-90 deg C, 2 h; 2.) reflux, 28 h
Note(s) (.COM): Multistep reaction
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538930
Reactant BRN (.RBRN): 635782, 6891040
Reactant (.RCT): glycine, chloromethyl-trifluoromethyl-phosphinic acid propyl ester

Product BRN (.PBRN): 2045054, 1731035
Product (.PRO): Carboxymethylamino-methylphosphonic acid,
trifluoromethane
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538930.1
Reaction Classification (.CL): Chemical behaviour
Reagent (.RGT): NaOH
Solvent (.SOL): ethanol, H2O
Temperature (.T): 20 Cel
Subject Studied (.SUBJ): Rate constant
Reference(s):

1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538929
Reactant BRN (.RBRN): 635782, 6890952
Reactant (.RCT): glycine, ethyl
(chloromethyl)(trifluoromethyl)phosphinate
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538929.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): 1.) 50percent NaOH
Other Conditions (.COND): 1.) water, 80-90 deg C, 2 h; 2.) reflux, 28 h
Note(s) (.COM): Multistep reaction
Reference(s):

1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538928
Reactant BRN (.RBRN): 635782, 6890952
Reactant (.RCT): glycine, ethyl
(chloromethyl)(trifluoromethyl)phosphinate
Product BRN (.PBRN): 2045054, 1731035
Product (.PRO): Carboxymethylamino-methylphosphonic acid,
trifluoromethane
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538928.1
Reaction Classification (.CL): Chemical behaviour
Reagent (.RGT): NaOH
Solvent (.SOL): ethanol, H2O
Temperature (.T): 20 Cel
Subject Studied (.SUBJ): Rate constant
Reference(s):

1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L.

N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538927
Reactant BRN (.RBRN): 635782, 6890760
Reactant (.RCT): glycine, methyl
(chloromethyl)(trifluoromethyl)phosphinate
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538927.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): 1.) 50percent NaOH
Other Conditions (.COND): 1.) water, 80-90 deg C, 2 h; 2.) reflux, 28 h
Note(s) (.COM): Yield given. Multistep reaction
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538926
Reactant BRN (.RBRN): 635782, 6890760
Reactant (.RCT): glycine, methyl
(chloromethyl)(trifluoromethyl)phosphinate
Product BRN (.PBRN): 2045054, 1731035
Product (.PRO): Carboxymethylamino-methylphosphonic acid, trifluoromethane
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538926.1
Reaction Classification (.CL): Chemical behaviour
Yield (.YDT): 49 percent (BRN=2045054), 98 percent (BRN=1731035)
Reagent (.RGT): NaOH
Solvent (.SOL): ethanol, H2O
Temperature (.T): 20 Cel
Subject Studied (.SUBJ): Rate constant
Reference(s):
1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 722-724, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(4), <1987>, 818-820; BABS-5881566

Reaction:

RX

Reaction ID (.ID): 3538503
Reactant BRN (.RBRN): 1811751, 635782
Reactant (.RCT): chloromethyl-phosphonothioic acid
dichloride, glycine
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3538503.1
 Reaction Classification (.CL): Preparation
 Yield (.YDT): 31 percent (BRN=2045054)
 Reagent (.RGT): NaOH
 Solvent (.SOL): H2O
 Time (.TIM): 40 hour(s)
 Other Conditions (.COND): Heating
 Reference(s):
 1. Golovanov, A. V.; Maslennikov, I. G.; Shubina, T. V.; Kirichenko, L. N.; Lavrent'ev, A. N., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 57, <1987>, 201-202, Zh.Obshch.Khim., CODEN: ZOKHA4, 57(1), <1987>, 231; BABS-5875863

Reaction:

RX

Reaction ID (.ID): 3369734
 Reactant BRN (.RBRN): 1209228, 605574, 635782
 Reactant (.RCT): formaldehyde, phosphonic acid dimethyl ester, glycine
 Product BRN (.PBRN): 969466, 6858490, 1884944, 2045054
 Product (.PRO): phosphonic acid monomethyl ester, N-(hydroxymethoxyphosphinyl)methyl-N-methylglycine, Glycindimethylphosphonsaeure, Carboxymethylamino-methylphosphonic acid
 No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 3369734.1
 Reaction Classification (.CL): Chemical behaviour
 Reagent (.RGT): NaOH
 Subject Studied (.SUBJ): Mechanism
 Reference(s):
 1. Strunin, B. P.; Khizbullin, F. F., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 58(10), <1988>, 1992-1996, Zh.Obshch.Khim., CODEN: ZOKHA4, 58(10), <1988>, 2238-2242; BABS-5882555

Reaction:

RX

Reaction ID (.ID): 2301646
 Reactant BRN (.RBRN): 3618985
 Reactant (.RCT): <(dimethoxy-phosphorylmethyl)-ethoxycarbonyl-amino>-acetic acid ethyl ester
 Product BRN (.PBRN): 2045054
 Product (.PRO): Carboxymethylamino-methylphosphonic acid
 No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 2301646.1
 Reaction Classification (.CL): Preparation
 Yield (.YDT): 73.4 percent (BRN=2045054)
 Reagent (.RGT): aq. HBr conc.
 Time (.TIM): 12 hour(s)
 Other Conditions (.COND): Heating
 Reference(s):
 1. Maier, Ludwig, Phosphorus, Sulfur Silicon Relat.Elem., CODEN: PSSLEC, 47, <1990>, 361-365; BABS-5510712

Reaction:

RX

Reaction ID (.ID): 2185714
Reactant BRN (.RBRN): 2965754
Reactant (.RCT): <(dimethoxy-phosphorylmethyl)-amino>-acetic acid
Product BRN (.PBRN): 2045054, 1946286, 1884944, 1811747
Product (.PRO): Carboxymethylamino-methylphosphonic acid, Methyl-N-phosphonomethylglycinat, Glycindimethylphosphonsaeure, hydroxymethyl-phosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 2185714.1
Reaction Classification (.CL): Preparation
Reagent (.RGT): HCl
Note(s) (.COM): Yield given. Yields of byproduct given
Reference(s):
1. Strunin, B. P.; Khizbullin, F. F., J.Gen.Chem.USSR (Engl.Transl.), CODEN: JGCHA4, 58(10), <1988>, 1992-1996, Zh.Obshch.Khim., CODEN: ZOKHA4, 58(10), <1988>, 2238-2242; BABS-5882555

Reaction:

RX

Reaction ID (.ID): 2178898
Reactant BRN (.RBRN): 2860219
Reactant (.RCT): N-benzyl-N-phosphonomethyl-glycine
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 2178898.1
Reaction Classification (.CL): Preparation
Yield (.YDT): 99 percent (BRN=2045054)
Reagent (.RGT): H2
Catalyst (.CAT): 5percent Pd/charcoal
Time (.TIM): 45 hour(s)
Other Conditions (.COND): Ambient temperature
Reference(s):
1. Maier, Ludwig, Phosphorus, Sulfur Silicon Relat.Elem., CODEN: PSSLEC, 61(1.2.), <1991>, 65-67; BABS-5592373

Reaction:

RX

Reaction ID (.ID): 2092661
Reactant BRN (.RBRN): 2113142
Reactant (.RCT): N-phosphonomethylglycine triethyl ester
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 2092661.1
Reaction Classification (.CL): Preparation
Yield (.YDT): 95.3 percent (BRN=2045054)
Reagent (.RGT): bee venom
Solvent (.SOL): various solvent(s)
Time (.TIM): 6 hour(s)
Temperature (.T): 37 Cel

Other Conditions (.COND): pH 8.7

Reference(s):

1. Natchev, Ivan A., Phosphorus Sulfur, CODEN: PREEDF, 37, <1988>, 133-142; BABS-5767534

Reaction:

RX

Reaction ID (.ID): 2041741
Reactant BRN (.RBRN): 1952653
Reactant (.RCT): N-(phosphonomethyl)-glycine, 1-ethyl ester
Product BRN (.PBRN): 2045054
Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 2041741.1
Reaction Classification (.CL): Preparation
Yield (.YDT): 80.2 percent (BRN=2045054)
Reagent (.RGT): .alpha.-chymotrypsin
Solvent (.SOL): various solvent(s)
Time (.TIM): 6 hour(s)
Temperature (.T): 25 Cel
Other Conditions (.COND): pH 7.8
Reference(s):
1. Natchev, Ivan A., Phosphorus Sulfur, CODEN: PREEDF, 37, <1988>, 133-142; BABS-5767534

Reaction:

RX

Reaction ID (.ID): 1963480
Reactant BRN (.RBRN): 1795744
Reactant (.RCT): phosphonomethylimino-di-acetic acid
Product BRN (.PBRN): 2045054, 4309989, 1209246, 1751206, 605365, 1701219
Product (.PRO): Carboxymethylamino-methylphosphonic acid, (formyl-phosphonomethyl-amino)-acetic acid, formic acid, methylaminomethyl-phosphonic acid, N,N-dimethyl-formamide, aminomethyl-phosphonic acid
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 1963480.1
Reaction Classification (.CL): Chemical behaviour
Reagent (.RGT): O2, CoSO4*7H2O
Solvent (.SOL): H2O
Temperature (.T): 85 Cel
Pressure (.P): 41371.8 Torr
Other Conditions (.COND): var. temp., pressure and reagents; deuterium isotope effect
Subject Studied (.SUBJ): Product distribution, Rate constant, Mechanism
Reference(s):
1. Riley, Dennis P.; Fields, Donald L.; Rivers, Willie, J.Amer.Chem.Soc., CODEN: JACSAT, 113(9), <1991>, 3371-3378; BABS-5536468

Reaction:

RX

Reaction ID (.ID): 1963478
Reactant BRN (.RBRN): 1795744
Reactant (.RCT): phosphonomethylimino-di-acetic acid
Product BRN (.PBRN): 2045054

Product (.PRO): Carboxymethylamino-methylphosphonic acid
No. of React. Details (.NVAR): 3

Reaction Details:

RX

Reaction RID (.RID): 1963478.1
Reaction Classification (.CL): Preparation
Yield (.YDT): 65 percent (BRN=2045054)
Reagent (.RGT): concd H2SO4, MnO2
Solvent (.SOL): H2O
Time (.TIM): 3 hour(s)
Other Conditions (.COND): Ambient temperature
Reference(s):
1. Krawczyk, Henryk; Bartczak, Tadeusz J., Phosphorus, Sulfur Silicon
Relat. Elem., CODEN: PSSLEC, 82(1-4), <1993>, 117-126; BABS-5846476

RX

Reaction RID (.RID): 1963478.2
Reaction Classification (.CL): Preparation
Yield (.YDT): 50 percent (BRN=2045054)
Reagent (.RGT): conc. sulfuric acid, H2O2
Solvent (.SOL): H2O
Time (.TIM): 6 hour(s)
Temperature (.T): 82 - 87 Cel
Reference(s):
1. Barsukov, A. V.; Matkovskaya, T. A.; Yaroshenko, G. F.; Allakhverdiv,
G. R.; Dyatlova, N. M., J. Gen. Chem. USSR (Engl. Transl.), CODEN: JGCHA4,
54, <1984>, 933-936, Zh. Obshch. Khim., CODEN: ZOKHA4, 54(5), <1984>,
1045-1048; BABS-5871201

RX

Reaction RID (.RID): 1963478.3
Reaction Classification (.CL): Preparation
Reagent (.RGT): sulfuric acid, H2O2
Reference(s):
1. Shkol'nikova, L. M.; Porai-Koshits, M. A.; Dyatlova, N. M.; Yaroshenko,
G. F.; Rudomino, M. V.; Kolova, E. K., J. Struct. Chem. (Engl. Transl.),
CODEN: JSTCAM, 23(5), <1982>, 737-746, Zh. Strukt. Khim., CODEN: ZSTKAI,
23(5), <1982>, 98-107; BABS-5878235

Reaction:

RX

Reaction ID (.ID): 1963477
Reactant BRN (.RBRN): 1795744
Reactant (.RCT): phosphonomethylimino-di-acetic acid
Product BRN (.PBRN): 2045054, 1946286
Product (.PRO): Carboxymethylamino-methylphosphonic acid,
Methyl-N-phosphonomethylglycinat
No. of React. Details (.NVAR): 1

Reaction Details:

RX

Reaction RID (.RID): 1963477.1
Reaction Classification (.CL): Chemical behaviour
Reagent (.RGT): O2, H2O, VOSO4, methylviologen chloride
salt
Time (.TIM): 200 min
Temperature (.T): 75 Cel
Pressure (.P): 10343 Torr
Other Conditions (.COND): var. reagents
Subject Studied (.SUBJ): Product distribution, Mechanism
Reference(s):
1. Riley, Dennis P.; Fields, Donald L., J. Amer. Chem. Soc., CODEN: JACSAT,
114(5), <1992>, 1881-1882; BABS-5595457

Reaction:

RX

Reaction ID (.ID):	1623964
Reactant BRN (.RBRN):	6896266, 1099706
Reactant (.RCT):	N-(hydroxymethyl)glycine sodium salt, phosphonic acid dibutyl ester
Product BRN (.PBRN):	2045054
Product (.PRO):	Carboxymethylamino-methylphosphonic acid

ACCESSION NUMBER: 1983:494448 CAPLUS
 DOCUMENT NUMBER: 99:94448
 TITLE: Transition element-containing crystalline aluminosilicate composition
 INVENTOR(S): Suzuki, Takashi; Hashimoto, Shoichiro; Nakano, Rieko; Orisaka, Masami
 PATENT ASSIGNEE(S): Mitsubishi Gas Chemical Co., Inc. , Japan
 SOURCE: Eur. Pat. Appl., 24 pp.
 CODEN: EPXXDW
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 70657	A1	19830126	EP 1982-303607	19820709
EP 70657	B1	19851204		
R: DE, FR, GB, IT, NL				
JP 58015023	A2	19830128	JP 1981-109869	19810714
JP 60052086	B4	19851118		
PRIORITY APPLN. INFO.:			JP 1981-109869	19810714

AB A transition-metal contg. aluminosilicate FZ-1 zeolite catalyst which can be regenerated after use by heating at apprx.380.degree. has .gtoreq.7 x-ray diffraction lines at angles of 7-25.degree., 0.07-80 wt.% transition metal in an elemental or compd. form and is prepd. by the hydrothermal reaction at 100-200.degree. of a shear-mixed aq. mixt. contg. Si, Al, F, water-sol. org. cation (e.g. quaternary ammonium), alkali, and transition metal compds. (or transition metal) with preferred mol ratios SiO₂/Al₂O₃ 100-3000, org. cation/SiO₂ 0.1-1.0 alkali/SiO₂ 0.15-0.7, F/SiO₂ 0.1-1.0, H₂O/SiO₂ 10-1000, transition metal/SiO₂ 0.003-0.3. The filtered and dried catalyst is calcined for 2-24 h at 350-800.degree.. Thus, sodium aluminate 3.3, NaOH 1.27, NH₄F 1.19, H₂O 146, Pr₄NBr 10.7 g, 30% SiO₂ sol 31.5, and Ni(OAc)₂.4H₂O 1.0 g were shear mixed and reacted at 150.degree. for 62 h in a sealed pressure vessel. The FZ-1 zeolite was calcined at 550.degree. for 5 h, treated with an 18% HCl soln. at 90.degree. for 5 h, washed free of Cl, and dried at 110.degree. for 10 h. The powder was kneaded with 20% SiO₂ sol, molded with a porous plate, and calcined at 550.degree. for 5 h. The calcined molded prouduct was ion exchanged at 90.degree. for 5 h with 10% NH₄Cl, cooled and cleaned, and calcined at 550.degree. for 4 h. The catalyst was placed in a reactor tube and used to generate hydrocarbons from a MeOH feed stock at 335.degree.. After 70 h of use the catalyst was well regenerated by heating at 380.degree. for 5 h.

=>

ACCESSION NUMBER: 1983:494448 CAPLUS
 DOCUMENT NUMBER: 99:94448
 TITLE: Transition element-containing crystalline aluminosilicate composition
 INVENTOR(S): Suzuki, Takashi; Hashimoto, Shoichiro; Nakano, Rieko; Orisaka, Masami
 PATENT ASSIGNEE(S): Mitsubishi Gas Chemical Co., Inc., Japan
 SOURCE: Eur. Pat. Appl., 24 pp.
 CODEN: EPXXDW
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
EP 70657	A1	19830126	EP 1982-303607	19820709
EP 70657	B1	19851204		
R: DE, FR, GB, IT, NL				
JP 58015023	A2	19830128	JP 1981-109869	19810714
JP 60052086	B4	19851118		

PRIORITY APPLN. INFO.: JP 1981-109869 19810714
 AB A transition-metal contg. aluminosilicate FZ-1 zeolite catalyst which can be regenerated after use by heating at .apprx.380.degree. has .gtoreq.7 x-ray diffraction lines at angles of 7-25.degree., 0.07-80 wt.% transition metal in an elemental or compd. form and is prepd. by the hydrothermal reaction at 100-200.degree. of a shear-mixed aq. mixt. contg. Si, Al, F, water-sol. org. cation (e.g. quaternary ammonium), alkali, and transition metal compds. (or transition metal) with preferred mol ratios SiO₂/Al₂O₃ 100-3000, org. cation/SiO₂ 0.1-1.0 alkali/SiO₂ 0.15-0.7, F/SiO₂ 0.1-1.0, H₂O/SiO₂ 10-1000, transition metal/SiO₂ 0.003-0.3. The filtered and dried catalyst is calcined for 2-24 h at 350-800.degree.. Thus, sodium aluminate 3.3, NaOH 1.27, NH₄F 1.19, H₂O 146, Pr₄NBr 10.7 g, 30% SiO₂ sol 31.5, and Ni(OAc)₂.4H₂O 1.0 g were shear mixed and reacted at 150.degree. for 62 h in a sealed pressure vessel. The FZ-1 zeolite was calcined at 550.degree. for 5 h, treated with an 18% HCl soln. at 90.degree. for 5 h, washed free of Cl, and dried at 110.degree. for 10 h. The powder was kneaded with 20% SiO₂ sol, molded with a porous plate, and calcined at 550.degree. for 5 h. The calcined molded prouduct was ion exchanged at 90.degree. for 5 h with 10% NH₄Cl, cooled and cleaned, and calcined at 550.degree. for 4 h. The catalyst was placed in a reactor tube and used to generate hydrocarbons from a MeOH feed stock at 335.degree.. After 70 h of use the catalyst was well regenerated by heating at 380.degree. for 5 h.

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US005095140A

United States Patent [19]
Fields, Jr.[11] **Patent Number:** **5,095,140**
[45] **Date of Patent:** **Mar. 10, 1992**[54] **PEROXIDE PROCESS FOR PRODUCING
N-PHOSPHONOMETHYLGLYCINE**[75] **Inventor:** Donald L. Fields, Jr., Manchester,
Mo.[73] **Assignee:** Monsanto Company, St. Louis, Mo.[21] **Appl. No.:** 684,745[22] **Filed:** Apr. 15, 1991**Related U.S. Application Data**[62] **Division of Ser. No. 542,995, Jun. 25, 1990, Pat. No.**
5,043,475.[51] **Int. Cl.⁵** C07F 9/38[52] **U.S. Cl.** 562/17[58] **Field of Search** 562/17[56] **References Cited****U.S. PATENT DOCUMENTS**

3,950,402	4/1976	Franz	260/502.5
3,954,848	5/1976	Franz	260/502.5
3,969,398	7/1976	Hershman	562/17
4,147,719	4/1979	Franz	562/17
4,853,159	8/1989	Riley et al.	562/17
4,952,723	8/1990	Fields et al.	562/17

4,965,402	10/1990	Riley et al.	562/17
4,983,764	1/1991	Pelyva et al.	562/17
5,023,369	6/1991	Fields	562/17

FOREIGN PATENT DOCUMENTS

2363634	6/1974	Fed. Rep. of Germany
0187347	7/1981	Hungary
2049697	12/1980	United Kingdom

Primary Examiner—Bruce Gray*Attorney, Agent, or Firm*—Frank D. Shearin

[57]

ABSTRACT

A process is provided for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid with a peroxide to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide. Thereafter, the N-phosphonomethyliminodiacetic acid-N-oxide is converted to N-phosphonomethylglycine by adding a catalytic amount of a metal selected from the group consisting of iron, zinc, aluminum, vanadium and copper, or a compound selected from the group consisting of water-soluble vanadium compounds, ferrous salts and cuprous salts.

5 Claims, No Drawings

PEROXIDE PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE

This is a division of application Ser. No. 07/542,995 filed June 23, 1990 now U.S. Pat. No. 5,043,475.

BACKGROUND OF THE INVENTION

This invention relates to a process for the preparation of N-phosphonomethylglycine, and more particularly to the preparation of N-phosphonomethylglycine by the conversion of N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine using peroxides.

N-Phosphonomethylglycine, known also by its common name glyphosate, is a highly effective, commercially important, phytotoxicant useful in controlling a large variety of weeds. It is applied to the foliage of a very broad spectrum of annual and perennial grasses and broadleaf plants. Industrial uses include control of weeds along roadsides, waterways, transmission lines, in storage areas, and in other nonagricultural areas. Usually, N-phosphonomethylglycine is formulated into herbicidal compositions in the form of its various salts in solution, preferably water.

U.S. Pat. No. 3,950,402 to Franz discloses a process for the production of N-phosphonomethylglycine by forming an admixture of N-phosphonomethyliminodiacetic acid, water, and a metallic catalyst selected from the noble metals, heating the admixture to an elevated temperature (greater than 70° C. to avoid low yields) and contacting the admixture with a free oxygen-containing gas.

U.S. Pat. No. 3,954,848 to Franz discloses a process for the production of N-phosphonomethylglycine by reacting N-phosphonomethyliminodiacetic acid with an oxidizing agent, such as hydrogen peroxide, in an aqueous acidic medium in the presence of a strong acid at a temperature of from about 70° C. to about 100° C. It is disclosed that one should employ at least 2 moles of the hydrogen peroxide for each mole of the N-phosphonomethyliminodiacetic acid, and preferably more.

Hungarian Patent Application No. 187,347 discloses a process for the preparation of N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid with peroxides using a catalytic amount of a metal compound selected from compounds of silver, iron, tin, lead, manganese or molybdenum. Molybdates are preferred. At temperatures lower than 80° C., usually a contaminated end product is obtained. Typically, the reaction is carried out at a temperature of above 80° C. and preferably above 100° C. at pressures exceeding atmospheric, wherein the intermediate N-oxide is decomposed as rapidly as it forms. It is further disclosed that two mole equivalents of peroxide should be used for each mole of N-phosphonomethyliminodiacetic acid to obtain acceptable yields of N-phosphonomethylglycine.

Although satisfactory results are obtained by the above processes to make N-phosphonomethylglycine, all of them suffer from one or more disadvantages, such as the use of excessive amounts of peroxide, the use of strong mineral acids and/or reaction at elevated temperatures and pressures. Now, there is provided a process which produces N-phosphonomethylglycine in high yields at modest temperatures and at atmospheric pressure using substantially stoichiometric amounts of peroxide to oxidize the N-phosphonomethyliminodiacetic acid to the desire N-phosphonomethylglycine

without using strong mineral acids, such as hydrochloric acid or sulfuric acid.

SUMMARY OF THE INVENTION

These and other advantages are achieved in a process for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid with peroxide to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide, the improvement which comprises adding a catalytic amount of a metal selected from the group consisting of iron, zinc, aluminum, vanadium and copper, or a compound selected from the group consisting of water-soluble vanadium salts, ferrous salts, and cuprous salts.

DETAILED DESCRIPTION OF THE INVENTION

The intermediate, N-phosphonomethyliminodiacetic acid-N-oxide, is known to those skilled in the art, and can be prepared by a number of methods. For example, the intermediate can be prepared by the teachings in U.S. Pat. No. 3,950,402 or U.S. Pat. No. 3,954,848, both to Franz. In Hungarian Patent Application 187,347, the intermediate is formed from N-phosphonomethyliminodiacetic acid using peroxides in the presence of compounds of silver, iron, tin, lead, manganese or molybdenum. In U.S. Pat. No. 4,062,669 to Franz, an N-organo-N-phosphonomethylglycine is oxidized with peroxide under acidic or basic conditions. Other methods may be known to those skilled in the art.

Any number of peroxides known to those skilled in the art can be used to prepare the N-phosphonomethyliminodiacetic acid-N-oxide. Suitable peroxides include hydrogen peroxide, performic acid, peracetic acid, perbenzoic acid, peroxytrifluoroacetic acid, benzoyl peroxide, benzenepersulfonic acid, and the like. Hydrogen peroxide is preferred, and it is advantageous to use hydrogen peroxide in the form of a concentrated solution, say between about 30% and 60%.

In the process of the present invention, it is preferred to prepare the N-phosphonomethyliminodiacetic acid-N-oxide by contacting N-phosphonomethyliminodiacetic acid with a peroxide in the presence of a catalytic amount of a water-soluble molybdenum compound or a water-soluble tungsten compound. A water-soluble tungsten compound is especially preferred.

The temperature of the process to prepare the N-phosphonomethyliminodiacetic acid-N-oxide can vary from as low as about 20° C. to about 70° C. Although temperatures below about 20° C. can be used, such temperatures would require the use of cooling, and no advantages are obtained. At temperatures above about 70° C., degradation of the N-phosphonomethyliminodiacetic acid-N-oxide is observed, which affects the final yield of the desire N-phosphonomethylglycine. Temperatures between about 20° C. and about 65° C. are preferred.

The salts of tungsten useful as catalysts to oxidize the N-phosphonomethyliminodiacetic acid to the N-phosphonomethyliminodiacetic acid-N-oxide are known to those skilled in the art. It is only necessary that the tungsten salts are soluble in the reaction medium. Suitable tungsten compounds include tungstic acid, 1,2-tungstophosphate, and barium tungstate. The alkali metal tungstates, such as sodium tungstate, potassium tungstate, and the like, provide satisfactory results, and the alkali metal tungstates are preferred.

The salts of molybdenum useful as catalysts to oxidize the N-phosphonomethyliminodiacetic acid to the N-phosphonomethyliminodiacetic acid-N-oxide are also known to those skilled in the art. It is only necessary that the molybdenum salts are soluble in the reaction medium. Suitable molybdenum compounds include molybdenum halides, such as molybdenyl trichloride and the like, alkali metal molybdates, such as sodium molybdate and the like, or more complex salts, such as the ammonium or alkali metal dimolybdates. Sodium and ammonium molybdates are preferred.

The amount of catalyst to convert the N-phosphonomethyliminodiacetic acid to the intermediate N-phosphonomethyliminodiacetic acid-N-oxide can vary within wide limits. Concentrations between about 0.01 and about 5 wt. % catalyst, based on the weight of the N-phosphonomethyliminodiacetic acid, provide satisfactory results. At concentrations of less than about 0.01 wt. % catalyst, the reaction is slow, and at concentrations greater than about 5 wt. %, no particular advantage is seen, although such higher concentrations are not harmful. It is preferred to use between about 0.01 wt. % and about 1 wt. % based on the weight of the N-phosphonomethyliminodiacetic acid.

In the process of the present invention, the amount of peroxide should be the stoichiometric amount required to convert the N-phosphonomethyliminodiacetic acid to the intermediate N-phosphonomethyliminodiacetic acid-N-oxide. As will occur to those skilled in the art, when less than the stoichiometric amount of peroxide is used, the yield of the desired N-phosphonomethylglycine is lower. A slight excess of peroxide can be used to insure a quantitative conversion of the N-phosphonomethyliminodiacetic acid to the intermediate, but there is no advantage to using large excesses of peroxide, and excesses of peroxide may be deleterious if water-soluble compounds, such as ferrous salts or cuprous salts, are used to convert the intermediate to N-phosphonomethylglycine.

Regardless of the method used to prepare the N-phosphonomethyliminodiacetic acid-N-oxide from the N-phosphonomethyliminodiacetic acid, the intermediate is contacted with a catalytic amount of a substance selected from the group consisting of iron metal, zinc metal, aluminum metal, vanadium metal or copper metal. Alternatively, a compound selected from the group consisting of the water-soluble salts of a vanadium compound, ferrous salts, and cuprous salts can convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to the desired N-phosphonomethylglycine. Suitable vanadium compounds that are soluble in the reaction mixture include vanadium pentoxide, vanadium sulfate, vanadium chloride and the like. Suitable water-soluble ferrous compounds that can be used in the process of the present invention include ferrous sulfate, ferrous halides, such as ferrous chloride, ferrous bromide and the like. Suitable water-soluble cuprous salts that can be used in the process of the present invention include cuprous chloride, cuprous bromide, cuprous sulfate and the like. Of the water-soluble compounds, vanadium compounds are preferred, and vanadyl sulfate is especially preferred.

The amount of catalyst to convert the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine depends upon the catalyst used and the amount of peroxide in excess of that required to produce the intermediate from the N-phosphonomethyliminodiacetic acid. When metals such as iron, zinc,

aluminum, vanadium and copper are used, the rate of reaction to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine depends upon the surface area of the metal present, and it is preferred to use from about 0.1 wt. % to about 10 wt. % of the metal, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide present. In addition, it is preferred to use the metal in any form that provides a high surface area, for example, a wool, a powder or finely divided granules. However, when a water-soluble compound is used as a catalyst, the excess peroxide will react with the water-soluble compound, and in addition to the amount of compound required to react with the excess peroxide, there should also be a sufficient amount of the water-soluble compound to catalyze the reaction of the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine. The amount of water-soluble compound remaining after reaction with the peroxide to act as a catalyst should be at least 0.005 wt. %, based on the amount of the N-phosphonomethyliminodiacetic acid-N-oxide. Excess water-soluble compound as high as 5%, or even higher, can be used, but there does not seem to be an advantage to using such higher concentrations for the conversion of the intermediate to N-phosphonomethylglycine, although such higher concentrations are not harmful. It is preferred to use between about 0.01 wt. % and about 2 wt. % of the water-soluble compound, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide, after reaction with any excess peroxides.

The temperature required to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to the desired N-phosphonomethylglycine can vary within wide limits. It is preferred to add the catalyst at or near room temperature (about 20° C.) because vigorous gas evolution frequently occurs, and the conversion of N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine is exothermic. It is preferred to keep the reaction temperature below about 80° C. by cooling the reaction vessel or using a low catalyst charge. Temperatures above about 80° C. will provide N-phosphonomethylglycine, but some yield loss may occur.

The concentration of the N-phosphonomethyliminodiacetic acid as the starting material can vary within wide limits in the process of the present invention. For example, an aqueous suspension containing up to 50 wt. % N-phosphonomethyliminodiacetic acid can be used. Higher concentrations of the N-phosphonomethyliminodiacetic acid can be used, but it can present processing difficulties because of the thickness of the slurry. On the other hand, an aqueous solution of the N-phosphonomethyliminodiacetic acid containing about 5 wt. % of the N-phosphonomethyliminodiacetic acid can also be used. Lower concentrations can also be used, but it requires processing large volumes of liquid in the process of the present invention. It is preferred to use an aqueous slurry containing from about 20 wt. % to about 40 wt. % of the N-phosphonomethyliminodiacetic acid.

The N-phosphonomethyliminodiacetic acid starting material can be prepared by methods known to those skilled in the art. For example, this material can be produced by the reaction of formaldehyde, iminodiacetic acid and orthophosphorous acid in the presence of sulfuric acid. Although the N-phosphonomethyliminodiacetic acid mixture resulting from this reac-

tion can be employed directly in the process of this invention, it is preferred to isolate the N-phosphonomethyliminodiacetic acid and then employ it herein.

This invention is further illustrated by, but not limited to, the following examples. Conversion is calculated by dividing the moles of other compounds produced by the moles of starting N-phosphonomethyliminodiacetic acid and multiplying by 100. Selectivity is calculated by dividing the moles of N-phosphonomethylglycine produced by the moles of N-phosphonomethyliminodiacetic acid converted and multiplying by 100.

EXAMPLE 1

This Example illustrates the process of the present invention using a water-soluble vanadium salt to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

(A) To a 100 ml round bottomed flask was added water (25 ml), N-phosphonomethyliminodiacetic acid (20 g), 47% hydrogen peroxide (7.1 g) and sodium tungstate (0.05 g). The mixture was heated to 65° C. and maintained at this temperature until a solution was obtained (about 58 minutes), indicating the N-oxide was formed. The solution was then allowed to cool to about 55° C. and stirred for an additional 30 minutes.

(B) After cooling to room temperature, vanadyl sulfate (0.05 g, 29% water content) was added to the solution. After stirring for about 5 minutes, the color of the solution changed from blue to light green. Gas evolution began with a slow exotherm. When the temperature reached about 40° C., the exotherm greatly accelerated to 65° C. and cooling water was applied to maintain the solution at this temperature. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrate and solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 96.7%, and the selectivity to N-phosphonomethylglycine was 91.4%.

EXAMPLE 2

This Example illustrates the process of the present invention using a water-soluble ferrous salt to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

The procedure of Example 1 Step (A) was repeated. Then after the solution was allowed to cool to room temperature, ferrous sulfate (0.02 g) was added to the solution. Gas evolution was observed, and the temperature of the solution rose to 65° C. Cooling water was applied to keep the temperature below 70° C. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrate and solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 99.5%, and the selectivity to N-phosphonomethylglycine was 93.7%.

EXAMPLE 3

This Example illustrates the process of the present invention using zinc metal to convert N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

(A) To a 100 ml round bottomed glass flask was added water (37 ml), N-phosphonomethyliminodiacetic acid (14.0 g), 30% hydrogen peroxide (7.2 g) and ammonium dimolybdate tetrahydrate (0.32 g). The mixture was heated to 65° C. and maintained at this temperature until a solution was obtained (about 30 minutes), indicating the N-oxide was formed. The solution was then allowed to cool to 45° C. and stirred for 50 minutes.

(B) After cooling to room temperature, zinc metal powder (0.4 g) was added to the solution. Vigorous gas evolution was observed, and the temperature of the solution rose to 55° C. in about a 10-minute period. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrate and solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 91.0%, and the selectivity to N-phosphonomethylglycine was 93.8%.

EXAMPLE 4

This Example illustrates the use of copper metal, aluminum metal, and a water-soluble cuprous salt to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

The procedure of Example 3 Step (A) was repeated. After cooling to room temperature, small aliquots of the solution containing the N-phosphonomethyliminodiacetic acid-N-oxide were taken and placed in 25 ml beakers. To one aliquot was added a copper penny. To another aliquot was added aluminum foil. To a third aliquot was added a small amount of cuprous chloride, and to a fourth aliquot was added vanadium metal. In all cases, gas evolution was observed, indicating that the intermediate N-phosphonomethyliminodiacetic acid-N-oxide was converted to N-phosphonomethylglycine.

Although the invention has been described in terms of specified embodiments which are set forth in considerable detail, it should be understood that this is by way of illustration only, and that alternative embodiments and operating techniques will become apparent to those skilled in the art in view of the disclosure. Accordingly, modifications can be made without departing from the spirit of the described invention.

What is claimed is:

1. A process for producing N-phosphonomethylglycine which comprises oxidizing N-phosphonomethyliminodiacetic acid with a peroxide to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide, and then adding a catalytic amount of a water-soluble vanadium compound to convert the intermediate to N-phosphonomethylglycine.

2. A process of claim 1 wherein the amount of catalyst to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine is between about 0.005 wt. % and about 5 wt. %, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide present.

3. A process of claim 2 wherein the amount of catalyst is between about 0.01 wt. % and about 2.0 wt. %.

4. A process of claim 1 wherein the catalyst is vanadyl sulfate.

5. A process of any of claims 4 wherein the peroxide is hydrogen peroxide.

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US005179228A

United States Patent [19]

Martin Ramon et al.

[11] **Patent Number:** 5,179,228[45] **Date of Patent:** Jan. 12, 1993

[54] **PREPARATION OF
N-PHOSPHONOMETHYLGLYCINE BY
OXIDATION OF
N-PHOSPHONOMETHYLIMINODIACETIC
ACID**

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PCT Pub. Date: Sep. 19, 1991

[51] **Int. Cl.⁵** C07F 9/38

[52] **U.S. Cl.** 562/17

[58] **Field of Search** 562/17

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Attorney, Agent, or Firm—Henry M. Bissell

[57] **ABSTRACT**

Improvements to a method for preparing N-phosphonomethylglycine by oxidation of N-phosphonomethyliminodiacetic acid. N-phosphonomethylglycine may be obtained by oxidation of N-phosphonomethyliminodiacetic acid with O₂ or with an oxygen-containing gas, in the presence of a noble metal catalyst on activated carbon. To avoid the catalyst losses, the improvements of the invention consist in a pressure scavaging with N₂, after completion of the oxidation reaction. Owing to such treatment, the catalyst losses are reduced from 30% to 1%, making the processing economically viable on a large industrial scale. The recovered catalyst holds its catalytic activity and may be reused at least 20 consecutive times. N-phosphonomethylglycine is a herbicide of extended application.

4 Claims, No Drawings

**PREPARATION OF
N-PHOSPHONOMETHYLGLYCINE BY
OXIDATION OF
N-PHOSPHONOMETHYLIMINODIACETIC ACID**

FIELD OF THE INVENTION

The invention relates to improvements introduced into a method of obtaining N-phosphonomethylglycine by oxidation of N-phosphonomethyliminodiacetic acid with oxygen or a gas containing oxygen, utilising as catalyst a noble metal supported on activated carbon. Specifically, the improvements of the invention relate to a treatment directed towards minimising the loss of the noble metal catalyst which occurs in this type of reaction.

ANTECEDENTS OF THE INVENTION

N-phosphonomethylglycine, described in the U.S. Pat. No. 3,799,758, is a known herbicide and its use is very widespread. Since its appearance on the market, various methods for obtaining it have been described and patented. One of these methods, specifically, the one claimed in the Spanish Patent No. 415.335 in the name of the Monsanto Company (equivalent to the U.S. Pat. No. 258,281, on May 5, 1972) provides a method of obtaining N-phosphonomethylglycine by oxidation of N-phosphonomethyliminodiacetic acid with oxygen or a gas containing oxygen, utilising a noble metal (Pd, Pt, Rh) supported on activated carbon as catalyst for the reaction. Although this method allows for obtaining N-phosphonomethylglycine in acceptable yield and state of purity, it has the disadvantage that the losses of the noble metal used as catalyst are so great (may be as much as 30%) that said method is not economically profitable and that the losses of the noble metal increase the price of the finished product to such an extent that the method is not viable on an industrial scale.

On the other hand, it is a fact known by the technical experts in catalysis that the losses of the noble metal which occur in the both acidic and basic catalytic methods, is by dissolution of said metal in the reaction water, thus requiring a complex and costly treatment to recover said metal. Consequently, this type of method is not viable in practice for obtaining finished products with slightly increased value.

Therefore it would be advantageous to have available a method which allows for obtaining N-phosphonomethylglycine of sufficient purity in good yield by oxidation of N-phosphonomethyliminodiacetic in the presence of a noble metal catalyst which overcomes the disadvantages referred to previously. In particular, it would be advantageous for this method to minimise the losses of noble metal used as catalyst in such a way that they do not substantially increase the cost of the finished product, with the object of rendering this method industrially viable.

Consequently, an object of the invention is the introduction of improvements over the known methods of obtaining N-phosphonomethylglycine by oxidation of N-phosphonomethyliminodiacetic acid with oxygen, in the presence of a noble metal supported on activated carbon as catalyst, providing that said improvements minimise the losses of noble metal, by means of implementation of a treatment intended to recover practically the total amount of the catalyst utilised, without loss of its catalytic activity.

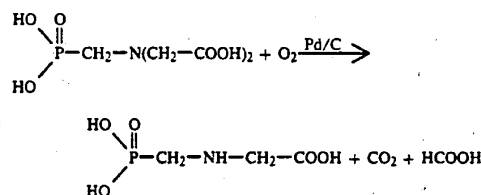
BRIEF DESCRIPTION OF THE INVENTION

The improvements of the invention may be stated as specifically to minimise the losses of the noble metal catalyst used for obtaining N-phosphonomethylglycine by oxidation of N-phosphonomethyliminodiacetic acid. For minimising these losses, the invention proposes effecting a flushing-out with nitrogen once the oxidation reaction is completed.

Due to this, it follows that the content of noble metal in the reaction solution is less than 1 ppm, compared with a content of said metal greater than 70 ppm which is present in said solution if the flushing-out with nitrogen is not effected. Therefore, this flushing-out with nitrogen minimises the losses, lowering the percentage loss from 30% to less than 1%, in this way making this type of method economically viable. The obtaining of these improvements will be referred to in detail in the following description.

**DETAILED DESCRIPTION OF THE
INVENTION**

The invention provides a series of betterments or improvements directed towards minimising the losses of noble metal used as catalyst in the known method for obtaining N-phosphonomethylglycine by oxidation of N-phosphonomethyliminodiacetic acid. In the prior Patent cited in the antecedents for the invention, a method for obtaining N-phosphonomethylglycine is described which may be characterised in accordance with the following equation in which, for the sake of simplicity, palladium on carbon Pd/C is used as the catalyst:



The reaction is carried out in the temperature range between 25° C. and 125° C., preferable between 90° C. and 105° C., at a pressure in the range between 1 and 5 kg/cm². However, for the reasons indicated previously, the method disclosed in said Patent is not viable on the industrial scale. In order for said method to become industrially viable, the losses of catalyst would need to be minimised.

Therefore an economical and simple form of said method has been sought to render it industrially viable. This has resulted from making use of the improvements provided by the present invention. These improvements consist of effecting a treatment of the reaction solution once the reaction has been completed to recover practically the total amount of the catalyst utilised, without alteration of its catalytic activity and capability of being re-utilised to catalyse this type of reaction without varying the yields. Consequently, in a first phase, the oxidation of N-phosphonomethyliminodiacetic acid with oxygen or a gas containing oxygen is carried out in the presence of a noble metal catalyst supported on activated carbon and, once this reaction is completed, the reaction solution obtained is flushed-out with nitrogen under pressure for the purpose of recovering the noble

metal in accordance with the method of operation to be described later.

For carrying on the oxidation reaction to completion, it has been found that it is advantageous to carry on said reaction at a temperature in the range between 100° C. and 105° C., at a pressure in the range between 3 and 4 kg/cm², using water as the solvent at a pH value in the range between 4 and 8, with the best results being obtained at a pH value close to 7.

The initial concentration of N-phosphonomethyliminodiacetic acid should be in the range between 4% and 15% by weight, preferably between 4% and 6% by weight, because higher concentrations diminish the yield from the reaction and lower concentrations diminish the productivity. The percentage of catalyst calculated with respect to the N-phosphonomethyliminodiacetic acid may be varied between 4% and 10% by weight, although with a mean percentage of 6% it is possible to obtain very good results. For implementation of this invention, palladium on carbon (Pd/C) has been used as the catalyst.

Once the oxidation reaction has been completed, with the object of minimising the loss of the noble metal, the treatment which follows, and which constitutes the improvement provided by the present invention, is carried out. Said treatment may be summed up as being that, in a single phase after completion of the reaction in an atmosphere of oxygen, or of a gas containing oxygen, the reaction solution obtained is de-pressurised and is flushed-out twice with nitrogen, with the object of removing as much oxygen as possible from the reaction solution. Following this, the reaction vessel is re-pressurised with nitrogen, at a pressure in the range between 0.5 kg/cm² and 5 kg/cm², preferably between 1 and 2 kg/cm² and, maintaining this pressure, the passage of nitrogen is continued at a flow rate from 10 to 30 liters/minute, during a period of time lasting from 15 minutes up to 1 hour. Obviously, the flow rate (liters/minute) of nitrogen depends upon the scale of the process. The period of time of passing-in the nitrogen is a function of the temperature of the reaction solution, which may be between 20° C. and 120° C., since the reaction mixture, when pressurised with nitrogen could heat up or, alternatively this treatment could be carried out at the temperature of the oxidation reaction without the necessity of heating the reaction solution. It has been found that, with a temperature of the reaction solution of 115° C., the period of time for the passage of nitrogen is 30 minutes in order to obtain a content of 0.9 ppm of palladium in said solution and that, at a temperature of 100° C., the period of time for the passage of nitrogen is 45 minutes in order to obtain a content of 0.6 ppm of palladium in said solution. When the content of palladium in the reaction solution is less than 1 ppm, determined by atomic absorption, the reaction vessel is de-pressurised, the catalyst is filtered off for later use and the filtrate obtained is concentrated in vacuo. The N-phosphonomethylglycine is obtained by recrystallisation.

If this treatment is not carried out, then the content of palladium in the reaction solution is greater than 70 ppm, as is evident in the examples which accompany this description. These losses of noble metal greater than 70 ppm lead to an increase in cost of the finished product beyond the limits of economic viability.

However, by means of the treatment, proposed by this invention of the reaction solution once the reaction is completed, the losses of noble metal in the solution are minimised, and make viable, in a simple manner, a

method which was not carried out in the procedures referred to earlier. Furthermore, the recovered catalyst maintains its catalytic activity and may be re-utilised at least for 20 consecutive times without loss of its activity and without altering the yields.

Consequently, by means of the improvements due to this invention, it is possible to obtain N-phosphonomethylglycine by oxidation of N-phosphonomethyliminodiacetic acid, at the industrial level with an adequate purity and yield and, furthermore, it is possible to recover the noble metal catalyst used, without loss of its catalytic activity by means of a simple treatment which does not require the installation of complex equipment.

The present invention will be clearly illustrated with the following examples which are not to be considered as limitative in any way.

EXAMPLE 1

In a stainless-steel (AISI 316) autoclave reactor of 40 liters capacity, there are introduced in the following order: 2.045 Kg of N-phosphonomethyliminodiacetic acid of 97% purity, 33.974 Kg of water at a pH value of ca. 7, and 121.5 grams of dry catalyst (commercial) of 5% palladium on carbon, which represents 6.075 grams of pure palladium by assay.

Following this, the passing in of oxygen is continued until an internal pressure of 3.6-3.8 kg/cm² is reached and the mixture heats up, maintaining the given pressure until a temperature of 100° C. is reached, having oxygen passed through the mixture at a flow rate of 2.5 liters/minute. The suspension is stirred continuously under these conditions for a period of 2 hours. When the stated period of time has elapsed, a sample is taken and, after the catalyst has been removed by filtration, is analysed for the content of N-phosphonomethyliminodiacetic acid and the ppm of palladium present, finding 110 ppm. When it is confirmed that at least 95% of the starting material has been converted, the supply of oxygen is cut off and the reactor is de-pressurised, changing over to pressurisation this time with nitrogen up to a pressure of 2 Kg/cm² and the reaction solution is heated to 115° C., maintaining this condition with bubbles of nitrogen through the reaction mixture at a flow rate of 24 liters/minute during a period of time of at least 30 minutes. When the treatment is completed and it has been shown that the reaction solution at this moment has a palladium content of less than 1 ppm (0.9 ppm), the preceding treatment is terminated and the reactor is de-pressurised, the catalyst is filtered off and the filtrate obtained is later concentrated in vacuo and the N-phosphonomethylglycine is obtained by re-crystallisation. The yield of N-phosphonomethylglycine having a degree of purity greater than 97% was 1.449 kg. (yield 96.4%).

EXAMPLE 2

This experiment was carried out to determine the influence of temperature on the process of recovery of the palladium dissolved in the reaction solution. The experiment was carried out with the same method utilised for the reaction in Example 1. With regard to the treatment after the reaction for recovery of the palladium, this was carried out at a temperature equal to that of the reaction (100° C.) and the time employed so that the dissolved palladium was less than 1 ppm (0.6 ppm) in the reaction water was 45 minutes.

The yield of N-phosphonomethylglycine having a degree of purity greater than 97% was 1.440 Kg (yield 95.6%).

Having described the object of the present invention, it is declared that what constitutes the essential nature of the same is that which is stated in the following Claims.

We claim:

1. Improvements introduced into a method of obtaining N-phosphonomethylglycine by oxidation of N-phosphonomethyliminodiacetic acid with oxygen or a gas containing oxygen, in the presence of a catalyst of noble metal supported on activated carbon, said improvements being characterised in that, once the reaction has been completed and before proceeding with its cooling, a flushing-out with nitrogen under slight pres-

sure is carried out, at a temperature equal to, or greater than that of the reaction, for a definite period of time, which determines the reduction of the losses of noble metal in the solution.

2. The improvements according to claim 1, characterised in that the passing-in of nitrogen is effected at a temperature in the range between 20° C. and 120° C.

3. The improvements according to claim 1, characterised in that the passing-in of nitrogen is carried on for a period of time lasting from 15 minutes up to 1 hour.

4. The improvements according to claim 1, characterised in that the pressure of the reaction solution during the passing-in of nitrogen is in the range between 0.5 kg/cm² and 5 kg/cm².

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US005948938A

United States Patent [19]

Nakano et al.

[11] **Patent Number:** **5,948,938**[45] **Date of Patent:** **Sep. 7, 1999**[54] **PROCESS FOR PREPARING N-PHOSPHONOMETHYLGLYCINE**[58] **Field of Search** 562/17; 558/169,
558/166[75] **Inventors:** Kunio Nakano, Kawasaki; Shuzi Sayama, Yamato; Yukio Hirayama, Kawasaki; Naohiko Ohashi, Tokyo, all of Japan[56] **References Cited****U.S. PATENT DOCUMENTS**4,397,676 8/1983 Bakel .
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5,043,475 8/1991 Fields, Jr. 567/17[73] **Assignee:** Sankyo Company, Limited, Tokyo, Japan*Primary Examiner*—Gary Geist
Assistant Examiner—Brian J. Davis
Attorney, Agent, or Firm—Frishauf, Holtz, Goodman, Langer & Chick, P.C.[21] **Appl. No.:** 08/944,029[22] **Filed:** Aug. 29, 1997**Related U.S. Application Data**

[63] Continuation of application No. PCT/JP96/00550, Mar. 7, 1996.

[30] **Foreign Application Priority Data**

Mar. 7, 1995 [JP] Japan 7-046005

[51] **Int. Cl.⁶** C07F 9/22[52] **U.S. Cl.** 562/17[57] **ABSTRACT**

A process for preparing N-phosphonomethylglycine, which comprises treating N-phosphonomethyliminodiacetic acid in the presence of water, activated carbon and hydrogen peroxide. This process is a safe and efficient process for preparing N-phosphonomethylglycine.

28 Claims, No Drawings

PROCESS FOR PREPARING N-PHOSPHONOMETHYLGLYCINE

This application is a continuation application of International Application PCT/JP96/00550 filed Mar. 7, 1996.

This invention relates to an improved process for preparing N-phosphonomethylglycine which has been utilized as a starting material or an intermediate of a N-phosphonomethylglycine salt which has widely been used as a herbicide.

BACKGROUND OF THE INVENTION

A number of processes for preparing N-phosphonomethylglycine (hereinafter abbreviated to PMG) using N-phosphonomethyliminodiacetic acid (hereinafter abbreviated to PMIDA) as a starting material, using water as a solvent and using an oxidizing agent and a catalyst may be mentioned. Among them:

- (a) a process in which, under ordinary pressure or under high pressure, molecular oxygen or gas containing said oxygen is used as an oxidizing agent and activated carbon is used as a catalyst is found in (1) Japanese Unexamined Patent Publication (KOKAI) No. Sho 50-160222, (2) Japanese Unexamined Patent Publication (KOKAI) No. Sho 56-18994 and (3) Japanese Unexamined Patent Publication (KOKAI) No. Sho 60-246328, (b) a process in which hydrogen peroxide is used as an oxidizing agent and an acid (an organic acid or an inorganic acid) is used as a catalyst is found in (4) Japanese Unexamined Patent Publication (KOKAI) No. Sho 49-48620 and (5) Japanese Unexamined Patent Publication (KOKAI) No. Hei 2-270891, and (c) a process in which hydrogen peroxide is used as an oxidizing agent and a metal compound is used as a catalyst is found in (6) Japanese Unexamined Patent Publication (KOKAI) No. Hei 4-224593, (7) Japanese Unexamined Patent Publication (KOKAI) No. Hei 4-210992, (8) Japanese Unexamined Patent Publication (KOKAI) No. Hei 4-224592 and (9) Japanese Unexamined Patent Publication (KOKAI) No. Hei 4-273885, respectively.

In the technique of (a), the reaction proceeds extremely slowly under ordinary pressure, whereas although the yield of the reaction is good under high pressure, pressure equipment is required. Further, it is necessary to pre-treat the activated carbon to be used. For these reasons, this technique leads to increase in cost.

In the technique of (b), an organic acid or an inorganic acid is used, so that the reaction apparatus might be corroded, and much time is required for disposal of the used acid.

In the technique of (c), a metal compound is used. Some metal compounds are harmful substances, so that disposal might be attended by difficulties or, when the possibility of contaminating the product PMG with a harmful catalyst is considered, a countermeasure should be taken in view of environmental problems.

Since the problems as described above are involved, it has been demanded to develop a safe and efficient preparation process.

DISCLOSURE OF THE INVENTION

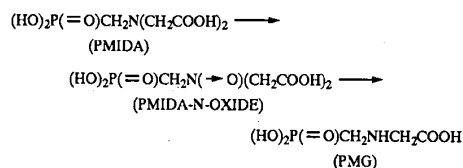
The present inventors have intensively studied a process which can solve the above problems and consequently PMG can be obtained safely and efficiently by treating PMIDA in the presence of water, activated carbon and hydrogen peroxide, to accomplish the present invention.

This finding is surprising. This is because it appears easy to achieve the present invention by selecting hydrogen peroxide as an oxidizing agent and activated carbon as a catalyst if the above prior techniques (a) and (b) are combined, but it has been believed in this field of the art that it is impossible to make such a selection.

That is, it has widely been known that activated carbon has a catalytic action in the decomposition of hydrogen peroxide and has been used as a reaction terminator. For example, there may be mentioned a technical book "Activated Carbon [written by John W. Hustler, translated by Takashi Oda and Yoshitomo Eguchi, page 220, line 2 to line 4 (Kyoritsu Shuppan Co.), Mar. 15, 1978, the third edition, the second impression]" or Japanese Unexamined Patent Publication (KOKAI) No. Sho 58-219193. In particular, in said patent publication (Example 6, page 9, lower left column, line 5), in preparation of a PMG guanidine salt, after hydrogen peroxide (H₂O₂) is added to a PMIDA guanidine salt to complete the reaction, activated carbon is added to the reaction mixture to decompose excess hydrogen peroxide. That is, it is described that activated carbon was used as a reaction terminator.

Therefore, if hydrogen peroxide and activated carbon are made to co-exist particularly under heating, hydrogen peroxide is immediately decomposed into water and oxygen, so that even if this system is applied to PMIDA, i.e., since this system belongs to the prior technique of the above (a), it could not be considered by a person skilled in the art to employ such a circuitous and disadvantageous process which is inferior to the process (a) even by using hydrogen peroxide and activated carbon. On the other hand, it has been found that when PMIDA is reacted under atmospheric pressure by using oxygen and activated carbon, the reaction proceeds extremely slowly, and the yield of PMG is low. However, it has been found unexpectedly that when PMIDA is reacted under atmospheric pressure by using hydrogen peroxide and activated carbon, the reaction proceeds extremely rapidly, and the desired PMG can be obtained in high yield. Not only it could not be supposed to employ such a combination, but also effects brought about by the combination are also quite unexpected.

It has been estimated that in the process of the present invention, since hydrogen peroxide and activated carbon are used, the following two stage reactions proceed.



However, actually, in the reaction of PMIDA and hydrogen peroxide, almost no PMIDA-N-oxide is detected during the reaction, and even when separately synthesized PMIDA-N-oxide is treated in the presence of activated carbon, almost no PMG is produced. Therefore, it is not certain whether PMG is produced by the above two stage reactions or not.

Anyway, it is estimated that in the present invention, hydrogen peroxide and PMIDA are activated by activated carbon to be easily converted into PMG.

In the following, the present invention is explained in more detail.

BEST MODE FOR PRACTICING THE INVENTION

PMIDA which is a starting material of the present invention can be prepared by a process well known in this field of the art, for example, reaction of formaldehyde, iminodiacetic acid and orthophosphorous acid in the presence of sulfuric acid (Japanese Unexamined Patent Publication (KOKAI) No. Sho 49-48620), a process in which iminodiacetic acid is reacted with formaldehyde and phosphorous acid in the presence of hydrochloric acid (Japanese Unexamined Patent Publication (KOKAI) No. Sho 50-160222) or a process in which phosphorus trichloride is added to an aqueous sodium iminodiacetate solution and the mixture is reacted with formaldehyde (Japanese Patent Publication (KOKOKU) No. Hei 5-37431). PMIDA to be provided for the present invention may be prepared by a process other than the above processes and is not particularly limited.

As the activated carbon to be used in the present invention, there may be used generally commercially available various kinds of activated carbons. Many kinds of activated carbons are commercially available. For example, when the activated carbons are classified according to a starting material, there may be mentioned activated carbons such as peat carbon using peat as a starting material, lignite carbon using brown coal or lignite as a starting material, coal carbon using bituminous coal or the like as a starting material, wood carbon and woody carbon using wood or a woody material as a starting material and coconut shell carbon using coconut shell as a starting material. Further, when they are classified according to a shape, there may be mentioned granulated carbon, granular carbon, pulverized carbon, powdered carbon, etc.

Examples of the activated carbon to be used in the present invention are shown below, but all of them cannot be shown. However, the activated carbon should not be limited thereto as a matter of course.

Granular Shirasagi Gc, Granular Shirasagi Cc, Granular Shirasagi Wc, Granular Shirasagi WHc, Granular Shirasagi LHc, Granular Shirasagi WHA, Granular Shirasagi GOC, Granular Shirasagi APRC, Granular Shirasagi TAC, Granular Shirasagi MAC, Granular Shirasagi XRC and Granular Shirasagi NCC, Granular Shirasagi KL, Granular Shirasagi DC, Granular Shirasagi Gx, Granular Shirasagi Sx, Granular Shirasagi Cx, X-7000, X-7100, Granular Shirasagi GHx, Granular Shirasagi GHxUG, Granular Shirasagi GS1x, Granular Shirasagi GS2x, Granular Shirasagi GTx, Granular Shirasagi GTSx, Granular Shirasagi Gx, Granular Shirasagi SRCx, MOLSIEVON 3A, MOLSIEVON 4A, MOLSIEVON 5A and ALDENITE, CARBORAFFIN, High Power Shirasagi, Purified Shirasagi, Special Shirasagi, Shirasagi A, Shirasagi M, Shirasagi C, Shirasagi P and Shirasagi PHC which are produced by Takeda Chemical Industries, Ltd.

BM-WA, BM-WD, BM-AL, BM-AH, BM-GB, BM-GA, BM-GCA, MM-CD, MM-CB, MM-CBS, GM-GB, GM-GA, GM-GH, GM-AS, GM-AA, PM-PA, PM-PW, PM-PW1, PM-WA, PM-KI, PM-YO, PM-KS, PM-MO, PM-AA, PM-PE, PM-CR, PM-WA, PM-SX, PM-FZ and PM-SAY which are produced by Mitsui Pharmaceuticals, Inc.

CAL, CPG, SGL, FILTRASORB 300, FILTRASORB 400, CANE CAL, APC, BPL, PCB, IVP, HGR, CP-4, FCA and Granular AL which are produced by Toyo Calgon Co.

Kuraraycoal GG, Kuraraycoal GS, Kuraraycoal GC, Kuraraycoal SA, Kuraraycoal KG, Kuraraycoal GM, Kuraraycoal GW, Kuraraycoal GL, Kuraraycoal GLC,

Kuraraycoal KW, Kuraraycoal GWC, Kuraraycoal PW, Kuraraycoal PW-W5, Kuraraycoal PK, Kuraraycoal YP, Kuraraycoal T-B, Kuraraycoal G-H, Kuraraycoal T-S, Kuraraycoal T-F and Kuraraycoal T-C which are produced by Kuraray Chemical Co.

Taiko TA, Taiko TS, Taiko TG, Taiko TM, Taiko GL30; Taiko GL30A, Taiko GF30A, Taiko GF50A, Taiko CW1303, Taiko CW130BR, Taiko CW130A, Taiko CW130AR, Taiko CW612G, Taiko CW816G, Taiko CG48B, Taiko CG48BR, Taiko CG48A, Taiko CG48AR, Taiko SG, Taiko SGP, Taiko SGA, Taiko S, Taiko FC, Taiko FCS, Taiko SA1000, Taiko K, Taiko KS, Taiko KW-50, Taiko K(A), Taiko A, Taiko M, Taiko AP, Taiko RC, Taiko B5, Taiko P and Taiko W which are produced by Futamura Chemical Industry Co.

Tsurumicoal 4GS-S, Tsurumicoal 4G-2S, Tsurumicoal 4G-3S, Tsurumicoal 7GM, Tsurumicoal 4GM, Tsurumicoal 4GCX, Tsurumicoal SX, Tsurumicoal AX, Tsurumicoal MX, Tsurumicoal GOD, Tsurumicoal 4GM-X, Tsurumicoal 4GS-D, Tsurumicoal HC-6, Tsurumicoal HC-14, Tsurumicoal HC-20, Tsurumicoal HC-20C, Tsurumicoal HCA-S, Tsurumicoal 5GV, Tsurumicoal 4GV, Tsurumicoal GVA-S, Tsurumicoal HC-42, Tsurumicoal HC-30E, Tsurumicoal GL-30, Tsurumicoal HC-30X, Tsurumicoal 4GL, Tsurumicoal HC-30S, Tsurumicoal GL-30S, Tsurumicoal PA and Tsurumicoal PC which are produced by Tsurumi Coal Co.

NORIT PK, NORIT PKDA 10x30 MESH, NORIT ELORIT, NORIT AZO, NORIT GRANULAR DARCO, NORIT HYDRO DARCO, NORIT DARCO 8x30, NORIT DARCO 12x20 LI, NORIT DARCO 12x20 DC, NORIT PETRO DARCO, NORIT DARCO MRX, NORIT HYDRODARCO GCW, NORIT HYDRODARCO GCL, NORIT HYDRODARCO GTS, NORIT DARCO CF, NORIT DARCO VAPURE, NORIT DARCO GCV, NORIT C-GRANULAR, NORIT ROW, NORIT ROW 0.8 SUPRA, NORIT RO, NORIT ROX, NORIT ROX 0.8, NORIT RB, NORIT R, NORIT R. Extra, NORIT Sorbonorit, NORIT CAR, NORIT ROZ, NORIT RBAA, NORIT RBHG, NORIT RZN, NORIT RGM, NORIT SX, NORIT SX-ULTRA, NORIT SA, NORIT SA-1, NORIT D-10, NORIT PN, NORIT ZN, NORIT SA-AW, NORIT W, NORIT GL, NORIT CA, NORIT CA-1, NORIT CA-SP, NORIT CN, NORIT CG, NORIT DARCO KB, NORIT DARCO KBB, NORIT S-51, NORIT DARCO S-51, NORIT S-51-A, NORIT S-51FF, NORIT PREMIUM DARCO, NORIT DARCO GFP, NORIT HDC, NORIT HDR, NORIT HDH, NORIT GRO SAFE, NORIT FM-1, NORIT DARCO TRS and NORIT DARCO FGD which are available from Nippon Norit Co.

The amount of the activated carbon to be used may be 0.1 part by weight or more, preferably 0.1 to 0.75 part by weight, most preferably 0.1 to 0.4 part by weight based on 1 part by weight of PMIDA. If the amount is less than 0.1 part by weight, the reaction is not completed, and further side reaction occurs to lower purity, whereby the object of the present invention cannot be achieved. If it exceeds 0.75 part by weight, bad influence is not particularly exerted on quality and yield, but an effect to be brought about by use thereof cannot be expected, and it is not economical. The object can be achieved by powdery activated carbon in a smaller amount as compared with granular activated carbon.

The great characteristic of the activated carbon to be used in the present invention resides in that after it is used in the first reaction and recovered, it can be recycled as such any number of times for the second reaction and reactions subsequent thereto without regeneration treatment such as

activation. When the activated carbon is used repeatedly, its activity as a catalyst is not lowered, which is extremely economical. When the activated carbon is lost in operation such as filtration by using the activated carbon repeatedly, the lost amount thereof may be replenished.

As the hydrogen peroxide to be used in the present invention, a generally commercially available 30 to 60% by weight aqueous solution may be used, and it is not necessary to further dilute the solution with water.

The amount of the hydrogen peroxide to be used may be 2 moles or more, preferably 2 to 5 moles, most preferably 2.0 to 2.5 moles based on 1 mole of PMIDA. If the amount is less than 2 moles, the reaction is not completed, and a large amount of PMIDA remains as an unreacted compound. If it exceeds 5 moles, bad influence is not particularly exerted on quality and yield, but an effect to be brought about by use thereof cannot be expected and it is not economical.

The reaction of PMIDA and hydrogen peroxide in the present invention is an exothermic reaction, and the time of adding hydrogen peroxide varies depending on the cooling performance of the equipment, but it may be in the range which can remove the heat of reaction. The reaction proceeds rapidly by adding hydrogen peroxide, so that a long reaction time is not required and it is easy to control the reaction. The end point of said reaction can be determined by monitoring disappearance of PMIDA. The reaction of the present invention is completed in about 30 minutes to about 4 hours if the cooling performance of the reaction equipment is sufficient.

The reaction in the present invention proceeds in the presence of water. The amount of water may be any amount so long as the reaction mixture can be stirred. It may not be an amount which is sufficient for dissolving PMIDA or PMG and is not particularly limited. In general, it may be 1 part by weight or more, preferably 2 to 10 parts by weight based on 1 part by weight of PMIDA.

The reaction temperature in the present invention is preferably 50 to 90° C., and a further preferred temperature range is 60 to 80° C. If the temperature is 50° C. or lower, the progress of the reaction is slow, while if it exceeds 90° C., a by-product is produced to lower the purity and yield of the desired compound.

The pressure for practicing the present invention is not particularly limited so long as it is in the range for achieving the object of the present invention, and the present invention is practiced under pressure lower than atmospheric pressure, atmospheric pressure or pressure higher than atmospheric pressure. However, it is not particularly necessary to practice the present invention under pressure lower than atmospheric pressure or pressure higher than atmospheric pressure, and atmospheric pressure is sufficient. It is not necessary to use an expensive and dangerous autoclave requiring complicated operation, which is necessary in a process in which activated carbon and oxygen-containing gas are used in combination.

In the present invention, depending on the amount of water used, after completion of the reaction, the produced PMG is precipitated in a crystalline state or is dissolved to give an aqueous solution. There are various methods for isolating PMG as crystals, and there may be mentioned, for example, the following operation methods.

Isolation method (A): When the amount of water used is more than an amount which is necessary for dissolving the produced PMG, for example, the amount is 15 times by weight or more the amount of the charged PMIDA, the

reaction mixture is heated to suitable temperature or higher, for example, 80° C. or higher, preferably 85 to 90° C. and filtered under heating to separate activated carbon by filtration. The filtrate is concentrated under reduced pressure to an amount of suitable times, for example, 3.5 times by weight the amount of the charged PMIDA to isolate PMG crystals by crystallization.

Isolation method (B): When the amount of water used is less than an amount which is necessary for dissolving the produced PMG, for example, the amount is less than 15 times by weight the amount of the charged PMIDA, the reaction mixture is cooled to low temperature, for example, about 5° C., and the precipitated PMG and activated carbon are separated by filtration. A mixed cake comprising these PMG crystals and the activated carbon is dissolved in hot water, for example, at 80° C. or higher, preferably 85 to 90° C. in an amount of suitable times, for example, 15 times by weight the amount of the charged PMIDA. Thereafter, the solution is filtered under heating to separate the activated carbon by filtration. The filtrate is concentrated under reduced pressure to an amount of suitable times, for example, 3.5 times by weight the amount of the charged PMIDA to isolate PMG crystals by crystallization.

Isolation method (C): In Isolation method (A) and Isolation method (B), filtration under heating is carried out to separate activated carbon by filtration, whereby a filtrate is obtained. To the filtrate is added a water-soluble organic solvent, for example, methanol, acetone or acetonitrile in an amount of suitable times or more, for example, once by volume or more the amount of the filtrate to isolate PMG crystals by crystallization. In Isolation method (C), the yield is increased by several % as compared with Isolation method (A) or Isolation method (B).

Isolation method (D): After completion of the reaction, to the reaction mixture is added an inorganic base, for example, alkali hydroxide, preferably sodium hydroxide, or an organic base, for example, an organic amine such as isopropylamine in an amount which is sufficient for producing a salt by reaction with the produced PMG to form a PMG salt, whereby an aqueous solution of the PMG salt is prepared. The solution is filtered to separate activated carbon by filtration, and the filtrate is made acidic with a mineral acid or the like to isolate PMG by crystallization.

PMG to be obtained by the process of the present invention is obtained at high levels of purity and yield which are satisfactory values as an industrial preparation process.

For practicing the present invention, there may be mentioned the following embodiments.

(1) A process for preparing PMG by adding hydrogen peroxide to PMIDA, water and activated carbon while heating and stirring them.

(2) A process for preparing PMG by adding 2 to 5 moles of hydrogen peroxide based on 1 mole of PMIDA to PMIDA, water and activated carbon while heating and stirring them.

(3) A process for preparing PMG by adding 2.0 to 2.5 moles of hydrogen peroxide based on 1 mole of PMIDA to PMIDA, water and activated carbon while heating and stirring them.

(4) A process for preparing PMG by adding hydrogen peroxide to 1 part by weight of PMIDA, 0.1 to 0.75 part by weight of activated carbon and water while heating and stirring them.

(5) A process for preparing PMG by adding 2 to 5 moles of hydrogen peroxide based on 1 mole of PMIDA to 1 part

recovered activated carbon and water under atmospheric pressure while heating and stirring them.

As a preferred embodiment of the present invention, there may be mentioned the preparation processes of the above embodiments (2), (3), (5), (6), (8), (9), (11), (12), (14), (15), (17), (18), (20), (21), (23), (24), (26), (27), (29), (30), (32), (33), (35) and (36), and as the most preferred embodiment, there may be mentioned the preparation processes of the embodiments (9), (18), (27) and (36).

EXAMPLES

In the following, Examples of the process of the present invention are shown, but the present invention is not limited thereto. The net amount of PMG obtained (Net) shows a value calculated from the gross amount of crystals obtained by isolation (Gross) \times purity (the content of PMG), the yield shows a value calculated from (the net amount of PMG obtained/theoretical value of PMG obtained) \times 100, and the conversion rate shows a value calculated from (the content of the produced PMG (molar number)/the amount of the used starting material PMIDA (molar number)) \times 100, respectively. The content of PMG was quantified by high performance liquid chromatography (HPLC).

Example 1

To 100 ml of water were added 5 g of the activated carbons shown in Table 1 and 20.0 g (0.088 mole) of PMIDA, respectively. Under stirring, to the mixtures were added dropwise 20.0 g (0.176 mole, 2.0-fold mole/PMIDA) of 30% aqueous hydrogen peroxide at 60 to 65° C. over 3 hours while maintaining said temperature. After the resulting mixtures were allowed to react for 1 hour, crystals were isolated by Isolation method (B) to obtain the results shown in Table 1.

TABLE 1

Activated carbon	Gross amount obtained (g)	Purity (%)	Net amount obtained (g)	Yield (%)
(1) PM-KS	12.52	96.1	12.03	80.8
(2) PC	13.18	97.4	12.84	86.2
(3) Taiko KW-50	13.34	95.9	12.79	85.9
(4) Kuraraycoal PW-W5	13.02	97.7	12.72	85.4
(5) Purified Shirasagi	12.62	97.3	12.28	82.5
(6) NORIT SX-ULTRA	12.74	97.8	12.46	83.7
(7) NORIT CA-SP	12.77	98.4	12.57	84.4
(8) NORIT SA-1	13.02	98.2	12.79	85.9
(9) DARCO S-51	12.59	97.5	12.28	82.5
(10) Calgon Granular AL	12.75	98.2	12.52	84.1
(11) Taiko SG	12.88	97.8	12.60	84.6
(12) X-7100	12.29	95.1	11.69	78.5
(13) NORIT ROW 0.8 SUPRA	12.55	98.5	12.36	83.0
(14) NORIT ROW 0.8	12.61	98.3	12.40	83.3
(15) DARKO 8x30	12.56	98.0	12.31	82.7

In the table, (1) in the column of Activated carbon is produced by Mitsui Pharmaceuticals, Inc., (2) is produced by Tsurumi Coal Co., (3) and (11) are produced by Futamura Chemical Industry Co., (4) is produced by Kuraray Chemical Co., (5) and (12) are produced by Takeda Chemical Industries, Ltd., and (6) to (9) and (13) to (15) show products available from Nippon Norit Co.

Example 2

To 100 ml of water were added the activated carbons (products available from Nippon Norit Co.) shown in Table

2 and 20.0 g (0.088 mole) of PMIDA, respectively. Under stirring, to the mixtures were added dropwise 20.0 g (0.176 mole, 2.0-fold mole/PMIDA) of 35% aqueous hydrogen peroxide at 60 to 65° C. over 3 hours while maintaining said temperature. After the resulting mixtures were allowed to react for 15 minutes, crystals were isolated by Isolation method (B) to obtain the results shown in Table 2.

TABLE 2

Activated carbon		Gross amount obtained (g)	Purity (%)	Net amount obtained (g)	Yield (%)
(1) NORIT SA-1	1	6.72	96.0	6.45	43.3
(2) NORIT SA-1	2	12.63	98.2	12.40	83.3
(3) NORIT SA-1	3	12.95	98.2	12.72	85.4
(4) NORIT SA-1	4	13.08	98.0	12.82	86.1
(5) NORIT SA-1	5	13.14	97.9	12.86	86.4
(6) NORIT SA-1	8	13.13	97.4	12.79	85.9
	3	12.29	95.6	11.75	78.9
(7) NORIT ROW 0.8 SUPRA					
	4	12.68	98.2	12.45	83.6
(8) NORIT ROW 0.8 SUPRA					
	5	12.80	98.4	12.60	84.6
(9) NORIT ROW 0.8 SUPRA					
	6	12.85	97.9	12.58	84.5
(10) NORIT ROW 0.8 SUPRA					
	7	12.91	98.3	12.69	85.2
(11) NORIT ROW 0.8 SUPRA					
	8	12.87	98.1	12.63	84.8
(12) NORIT ROW 0.8 SUPRA					
	15	12.94	97.8	12.66	85.0
(13) NORIT ROW 0.8 SUPRA					

Example 3

To 100 ml of water were added 5 g of activated carbon (NORIT ROW 0.8 SUPRA) and 20.0 g (0.088 mole) of PMIDA. Under stirring, to the mixture were added dropwise the 35% aqueous hydrogen peroxides shown in Table 3 at 60 to 65° C. over 3 hours, respectively, while maintaining said temperature. After the resulting mixtures were allowed to react for 1 hour, crystals were isolated by Isolation method (B) to obtain the results shown in Table 3.

TABLE 3

Hydrogen peroxide (based on mole of PMIDA)	Gross amount obtained (g)	Purity (%)	Net amount obtained (g)	Yield (%)
(1) 15.0 g, 0.154 mole (1.75 times)	10.19	95.0	9.68	65.0
	12.69	97.6	12.39	83.2
(2) 17.1 g, 0.176 mole (2.0 times)	12.79	97.9	12.52	84.1
(3) 19.3 g, 0.198 mole (2.25 times)	12.65	97.7	12.36	83.0
(4) 21.4 g, 0.220 mole (2.5 times)	12.65	98.0	12.40	83.3
(5) 42.8 g, 0.441 mole (5.0 times)				

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Example 4

To the amounts of water shown in Table 4 were added 5 g of activated carbon (NORIT ROW 0.8 SUPRA) and 20.0 g (0.088 mole) of PMIDA, respectively. Under stirring, to the mixtures were added dropwise 20.0 g (0.176 mole, 2.0-fold mole/PMIDA) of 30% aqueous hydrogen peroxide at 60 to 65° C. over 3 hours while maintaining said temperature. After the resulting mixtures were allowed to react for 1 hour, crystals were isolated by the isolation methods shown in Table 4, respectively, to obtain the results shown in Table 4.

TABLE 4

Water (g)	Isolation method	Gross amount obtained (g)	Purity (%)	Net amount obtained (g)	Yield (%)
(1)	10 Stirring was impossible	—	—	—	—
(2)	20 (B)	12.26	97.9	12.00	80.6
(3)	40 (B)	12.69	97.6	12.39	83.2
(4)	100 (B)	12.55	98.5	12.36	83.0
(5)	200 (B)	12.53	98.4	12.33	82.8
(6)	300 (A)	12.57	98.4	12.37	83.1
(7)	400 (A)	12.53	98.5	12.34	82.9

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TABLE 5

Temperature (° C.)	Gross amount obtained (g)	Purity (%)	Net amount obtained (g)	Yield (%)
(1) 25 to 30	9.46	71.9	6.80	45.7
(2) 40 to 45	10.96	76.7	8.41	56.5
(3) 50 to 55	11.53	97.7	11.26	75.6
(4) 60 to 65	12.55	98.5	12.36	83.0
(5) 70 to 75	12.48	98.6	12.31	82.7
(6) 80 to 85	12.39	98.6	12.22	82.1
(7) 90 to 95	11.98	98.4	11.79	79.2
(8) Reflux temperature	6.71	98.0	6.58	44.2

Example 6

To the amounts of water shown in Table 6 were added 2 g or 8 g of activated carbon (NORIT SA-1) and 20.0 g (0.088 mole) of PMIDA, respectively. Under stirring, to the mixtures were added dropwise 17.1 g (0.176 mole, 2.0-fold mole/PMIDA) or 19.7 g (0.203 mole, 2.3-fold mole/PMIDA) of 35% aqueous hydrogen peroxide at 60 to 65° C. over 3 hours while maintaining said temperature. After the resulting mixtures were allowed to react for 1 hour, crystals were isolated by Isolation method (B) to obtain the results shown in Table 6.

TABLE 6

Water (g)	Activated carbon (g)	Hydrogen peroxide	Gross amount obtained (g)	Purity (%)	Net amount obtained (g)	Yield (%)
(1) 40	2	17.1 g (2.0-fold mole)	12.78	97.2	12.40	83.3
(2) 40	8	17.1 g (2.0-fold mole)	12.89	96.8	12.48	83.8
(3) 40	2	19.7 g (2.3-fold mole)	12.75	97.5	12.43	83.5
(4) 40	8	19.7 g (2.3-fold mole)	12.77	98.0	12.51	84.0
(5) 200	2	17.1 g (2.0-fold mole)	12.47	98.2	12.25	82.3
(6) 200	8	17.1 g (2.0-fold mole)	12.60	97.7	12.31	82.7
(7) 200	2	19.7 g (2.3-fold mole)	12.48	97.9	12.22	82.1
(8) 200	8	19.7 g (2.3-fold mole)	12.62	98.2	12.39	83.2

Example 5

To 100 ml of water were added 5 g of activated carbon (NORIT ROW 0.8 SUPRA) and 20.0 g (0.088 mole) of PMIDA. Under stirring, to the mixture were added dropwise 20.0 g (0.176 mole, 2.0-fold mole/PMIDA) of 30% aqueous hydrogen peroxide at the temperatures shown in Table 5 over 3 hours, respectively, while maintaining said temperatures. The reaction time was 8 hours and 30 minutes in the case of employing a reaction temperature of 25 to 30° C. or 1 hour in the case of employing the other reaction temperatures. Thereafter, crystals were isolated by Isolation method (B) to obtain the results shown in Table 5.

Example 7

To the amounts of water shown in Table 7 were added 2 g or 8 g of activated carbon (NORIT SA-1) and 20.0 g (0.088 mole) of PMIDA, respectively. Under stirring, to the mixtures were added dropwise 17.1 g (0.176 mole, 2.0-fold mole/PMIDA) or 19.7 g (0.203 mole, 2.3-fold mole/PMIDA) of 35% aqueous hydrogen peroxide at 80 to 85° C. over 3 hours while maintaining said temperature. After the resulting mixtures were allowed to react for 1 hour, crystals were isolated by Isolation method (B) to obtain the results shown in Table 7.

TABLE 7

Water (g)	Activated carbon (g)	Hydrogen peroxide	Gross amount obtained (g)	Purity (%)	Net amount obtained (g)	Yield (%)
(1) 40	2	17.1 g (2.0-fold mole)	12.82	97.8	12.54	84.2
(2) 40	8	17.1 g (2.0-fold mole)	12.76	97.4	12.43	83.5
(3) 40	2	19.7 g (2.3-fold mole)	12.84	98.0	12.58	84.5
(4) 40	8	19.7 g (2.3-fold mole)	12.85	98.1	12.61	84.7
(5) 200	2	17.1 g (2.0-fold mole)	12.64	98.3	12.43	83.5
(6) 200	8	17.1 g (2.0-fold mole)	12.66	98.4	12.46	83.7
(7) 200	2	19.7 g (2.3-fold mole)	12.62	97.8	12.34	82.9
(8) 200	8	19.7 g (2.3-fold mole)	12.74	98.2	12.51	84.0

Example 8

(1) The same reaction was carried out 5 times by using only the activated carbon which was used in the reaction (1) of Example 6 and recovered. (2) The same reaction was carried out 10 times by using only the activated carbon which was used in the reaction (2) of Example 6 and recovered. (3) The same reaction was carried out 5 times by using only the activated carbon which was used in the reaction (7) of Example 7 and recovered. (4) The same reaction was carried out 10 times by using only the activated carbon which was used in the reaction (8) of Example 7 and recovered. The respective results are shown in Table 8.

TABLE 8

Water (g)	Hydrogen peroxide	Gross amount obtained (g)	Purity (%)	Net amount obtained (g)	Yield (%)
(1) 40	17.1 g (2.0-fold mole)	12.52	98.3	12.31	82.7
(2) 40	17.1 g (2.0-fold mole)	12.67	98.1	12.43	83.5
(3) 200	19.7 g (2.3-fold mole)	12.59	98.5	12.40	83.3
(4) 200	19.7 g (2.3-fold mole)	12.64	98.3	12.43	83.5

In the table, (1) and (3) show the results of the fifth reactions and (2) and (4) show the results of the tenth reactions, respectively.

COMPARATIVE EXAMPLES

Comparative Example 1

To 100 ml of water were added 5.0 g of activated carbon (NORIT SX-ULTRA) and 20.0 g (0.088 mole) of PMIDA. Under stirring, into the mixture was introduced oxygen gas at 60 to 65° C. for 8 hours at a flow rate of 46 ml/min (11.2-fold mole/PMIDA). Then, sodium hydroxide was added to the resulting mixture to form a PMG salt, whereby an aqueous solution of the PMG salt was prepared. The solution was filtered to separate the activated carbon by filtration, and PMG was quantified by HPLC to find that the amount produced was 3.66 g (0.0216 mole)(conversion rate: 24.6%).

Comparative Example 2

A 300 ml pressure glass container was charged with 100 ml of water, 1.5 g of activated carbon (NORIT SX-ULTRA)

and 5.0 g (0.022 mole) of PMIDA. Under stirring, into the mixture was introduced air at 60 to 65° C. for 7 hours under pressurization of 5 kg/cm² at an outlet rate of 15 ml/min. Then, the activated carbon was separated by filtration, and the filtrate was concentrated to 12 ml under reduced pressure to obtain 3.06 g of precipitated crystals (purity: 87.6%, yield: 72.0%).

Comparative Example 3

To 100 ml of water were added 5 g of 5% palladium carbon (produced by Kojima Chemical Co.) and 20.0 g (0.088 mole) of PMIDA. Under stirring, into the mixture was introduced oxygen gas at 60 to 65° C. for 6 hours at a flow rate of 51 ml/min (9.3-fold mole/PMIDA). Then, sodium hydroxide was added to the resulting mixture to form a PMG salt, whereby an aqueous solution of the PMG salt was prepared. The solution was filtered to separate the palladium carbon by filtration, and PMG was quantified by HPLC to find that the amount produced was 0.69 g (0.004 mole) (conversion rate: 4.5%).

Comparative Example 4

A 300 ml pressure glass container was charged with 100 ml of water, 5 g of 5% palladium carbon (produced by Kojima Chemical Co.) and 20.0 g (0.088 mole) of PMIDA. Under stirring, into the mixture was introduced air at 60 to 65° C. for 7 hours under pressurization of 5 kg/cm² at a flow rate of 20 ml/min. Then, sodium hydroxide was added to the resulting mixture to form a PMG salt, whereby an aqueous solution of the PMG salt was prepared. The solution was filtered to separate the palladium carbon by filtration, and PMG was quantified by HPLC to find that the amount produced was 2.92 g (0.0173 mole)(conversion rate: 19.7%).

Comparative Example 5

To 22 ml of water were added 10.7 g of conc. sulfuric acid and 20.0 g (0.088 mole) of PMIDA. Under stirring, to the mixture were added dropwise 23.9 g (0.211 mole) of 30% aqueous hydrogen peroxide at 90 to 95° C. over 4 hours while maintaining said temperature. The resulting mixture was allowed to react for 1 hour and then cooled to room temperature. Thereafter, 30.2 g of 28% sodium hydroxide was added to the mixture to neutralize the sulfuric acid, and the resulting mixture was cooled to 5° C. to obtain 8.10 g of precipitated crystals (purity: 93.2%, yield: 50.7%).

Comparative Example 6

To 15 ml of water were added 0.31 g of ammonium molybdate and 13.7 g (0.060 mole) of PMIDA. Under

stirring, to the mixture were added dropwise 6.0 g (0.062-fold mole) of 35% aqueous hydrogen peroxide at 60 to 65° C. over 15 minutes while maintaining said temperature. The resulting mixture was allowed to react for 50 minutes and then cooled to room temperature. Next, when an aqueous solution obtained by dissolving 0.24 g of sodium pyrosulfite in 5 g of water was added to the above reaction mixture, the resulting mixture was foamed and also the temperature thereof was raised to 65° C. Then, the mixture was cooled to obtain 8.35 g of precipitated crystals (purity: 68.3%, yield: 55.9%).

Comparative Example 7

To 100 ml of water were added 20.0 g (0.088 mole) of PMIDA. Under stirring, to the mixture were added 20.0 g (0.176 mole) of 30% aqueous hydrogen peroxide at 60 to 65° C. over 3 hours while maintaining said temperature. After the resulting mixture was allowed to react for 1 hour, sodium hydroxide was added to the mixture to form a PMG salt, whereby an aqueous solution of the PMG salt was prepared. PMG was quantified by HPLC to find that the amount was 2.7 g (0.0160 mole) (conversion rate: 18.2%).

From Comparative examples described above, the following facts can be indicated.

From Comparative example 1, even when activated carbon is used and oxygen is introduced for a long time (8 hours) under atmospheric pressure, only a small amount of PMG can be obtained.

From Comparative example 2, when activated carbon is used and air is introduced for a long time (7 hours) under pressurization (5 kg/cm²), PMG can be obtained efficiently.

From Comparative example 3, even when palladium carbon is used and oxygen is introduced for a long time (6 hours) under atmospheric pressure, only an extremely small amount of PMG can be obtained.

From Comparative example 4, even when palladium carbon is used and air is introduced for a long time (7 hours) under pressurization (5 kg/cm²), only a small amount of PMG can be obtained.

From Comparative example 5, even when reaction is carried out by using hydrogen peroxide and conc. sulfuric acid under atmospheric pressure, yield of PMG is low.

From Comparative example 6, when reaction is carried out by using hydrogen peroxide, molybdenum and sodium pyrosulfite under atmospheric pressure, the reaction mixture is foamed vigorously, and the temperature thereof is increased, thereby the reaction can be controlled with difficulty, and the yield of PMG is low.

From Comparative example 7, when PMIDA is reacted with hydrogen peroxide under atmospheric pressure, only a small amount of PMG can be obtained.

As compared with the prior art, the process of the present invention can be carried out under atmospheric pressure, so that pressure equipment is not required. Since no acid is used, there is no such problem as corrosion of the reaction apparatus, and since a metal compound in which a harmful compound might be contained is not used as a catalyst, there is not required intricate disposal for such a compound, and the process of the present invention can be carried out safely. It is easy to control the reaction, and the used activated carbon can be recycled any number of times without regeneration treatment. The desired compound of the present invention can be obtained in good purity and yield, and the process of the present invention is suitable as an industrial preparation process.

What is claimed is:

1. A process for preparing a N-phosphonomethylglycine, which comprises contacting N-phosphonomethyliminodiacetic acid with water, activated carbon and hydrogen peroxide.

2. The process according to claim 1, wherein the hydrogen peroxide is in an amount of at least 2 moles based on 1 mole of the N-phosphonomethyliminodiacetic acid and the activated carbon is in an amount of 0.1 part by weight based on 1 part by weight of the N-phosphonomethyliminodiacetic acid.

3. The process according to claim 2, wherein the hydrogen peroxide is in an amount of 2 to 5 moles based on 1 mole of the N-phosphonomethyliminodiacetic acid.

4. The process according to claim 2, wherein the hydrogen peroxide is in an amount of 2.0 to 2.5 moles based on 1 mole of the N-phosphonomethyliminodiacetic acid.

5. The process according to claim 2, wherein the activated carbon is in an amount of 0.1 to 0.75 part by weight based on 1 part by weight of the N-phosphonomethyliminodiacetic acid.

6. The process according to claim 2, wherein the activated carbon is in an amount of 0.1 to 0.4 part by weight based on 1 part by weight of the N-phosphonomethyliminodiacetic acid.

7. The process according to claim 2, wherein the activated carbon comprises activated carbon which is recovered from the process.

8. The process according to claim 2, wherein said process is carried out under atmospheric pressure.

9. The process according to claim 4, wherein the activated carbon is in an amount of 0.1 to 0.4 part by weight based on 1 part by weight of the N-phosphonomethyliminodiacetic acid.

10. The process according to claim 9, wherein the water is in an amount of 2 to 10 parts by weight based on 1 part by weight of the N-phosphonomethyliminodiacetic acid.

11. The process according to claim 10, wherein said process is carried out for 30 minutes to 4 hours.

12. A process for preparing N-phosphonomethylglycine, which comprises adding hydrogen peroxide to N-phosphonomethyliminodiacetic acid, water and activated carbon under heating and agitating.

13. The process according to claim 12, wherein the hydrogen peroxide is in an amount of at least 2 moles based on 1 mole of the N-phosphonomethyliminodiacetic acid and the activated carbon is in an amount of at least 0.1 part by weight based on 1 part by weight of the N-phosphonomethyliminodiacetic acid.

14. The process according to claim 13, wherein the heating is carried out at a temperature of above 30° C.

15. The process according to claim 13, wherein the heating is carried out at a temperature of 50 to 90° C.

16. The process according to claim 13, wherein the heating is carried out at a temperature of 60 to 80° C.

17. The process according to claim 14, wherein the hydrogen peroxide is in an amount of 2 to 5 moles based on 1 mole of the N-phosphonomethyliminodiacetic acid.

18. The process according to claim 14, wherein the hydrogen peroxide is in an amount of 2 to 2.5 moles based on 1 mole of the N-phosphonomethyliminodiacetic acid.

19. The process according to claim 14, wherein the activated carbon is in an amount of 0.1 to 0.75 part by weight based on 1 part by weight of the N-phosphonomethyliminodiacetic acid.

20. The process according to claim 14, wherein the activated carbon is in an amount of 0.1 to 0.4 part by weight

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based on 1 part by weight of the N-phosphonomethyliminodiacetic acid.

21. The process according to claim 14, wherein the activated carbon comprises activated carbon which is recovered from the process.

22. The process according to claim 14, wherein said process is carried out under atmospheric pressure.

23. The process according to claim 22, wherein the water is in an amount of 2 to 10 parts by weight based on 1 part by weight of the N-phosphonomethyliminodiacetic acid.

24. The process according to claim 23, wherein said process is carried out for 30 minutes to 4 hours.

25. The process according to claim 16, wherein the hydrogen peroxide is in an amount of 2 to 2.5 moles based on 1 mole of the N-phosphonomethyliminodiacetic acid; the activated carbon is in an amount of 0.1 to 0.4 part by weight

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based on 1 part by weight of the N-phosphonomethyliminodiacetic acid; and the water is in an amount of 2 to 10 parts by weight based on 1 part by weight of the N-phosphonomethyliminodiacetic acid.

26. The process of claim 1, wherein the hydrogen peroxide is in the form of a 30 to 60% by weight hydrogen peroxide aqueous solution.

27. The process of claim 13, wherein the hydrogen peroxide is in the form of a 30 to 60% by weight hydrogen peroxide aqueous solution.

28. The process of claim 25, wherein the hydrogen peroxide is in the form of a 30 to 60% by weight hydrogen peroxide aqueous solution.

* * * * *



US005962729A

United States Patent [19]

Hayden et al.

[11] **Patent Number:** 5,962,729[45] **Date of Patent:** Oct. 5, 1999

[54] **METHOD FOR THE MANUFACTURE OF N-PHOSPHONOMETHYLGLYCINE FROM N-PHOSPHONOMETHYLIMINODIACETIC ACID USING A CATALYTIC CARBON**

3,969,398 7/1976 Hershman .

5,356,849 10/1994 Matviya 502/180

[75] **Inventors:** Richard A. Hayden; Thomas M. Matviya, both of Pittsburgh, Pa.

Primary Examiner—Gary Geist*Assistant Examiner*—Jean F Vollano*Attorney, Agent, or Firm*—Titus & McConomy LLP

[73] **Assignee:** Calgon Carbon Corporation, Pittsburgh, Pa.

[57] **ABSTRACT**[21] **Appl. No.:** 09/078,775[22] **Filed:** May 14, 1998[51] **Int. Cl.⁶** C07F 9/22[52] **U.S. Cl.** 562/17; 562/11; 562/16[58] **Field of Search** 562/11, 16, 17; 502/418

An improved process is provided for the manufacture of N-phosphonomethylglycine from N-phosphonomethyliminodiacetic acid in the presence of a molecular-oxygen containing gas utilizing a catalytically active carbonaceous char. The improvement is provided by the use of a carbonaceous char capable of rapidly decomposing hydrogen peroxide in an aqueous solution.

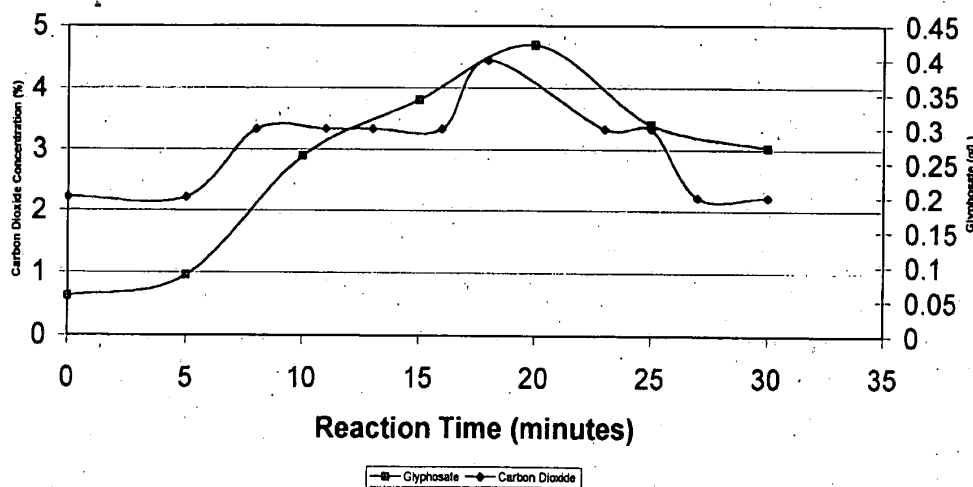
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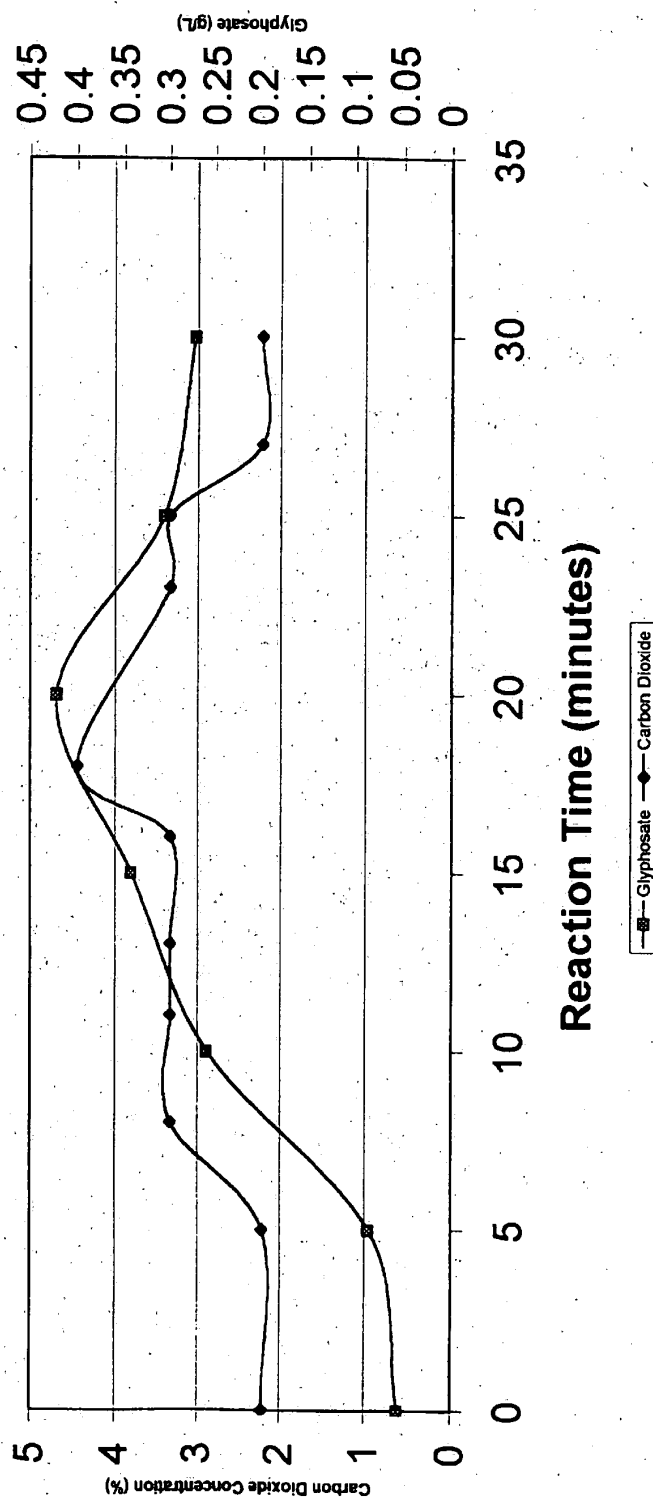
6 Claims, 2 Drawing Sheets

**Comparison Between Peak Carbon Dioxide
Concentration in Off-Gas with Peak Glyphosate
Concentration in Reactor Liquid**

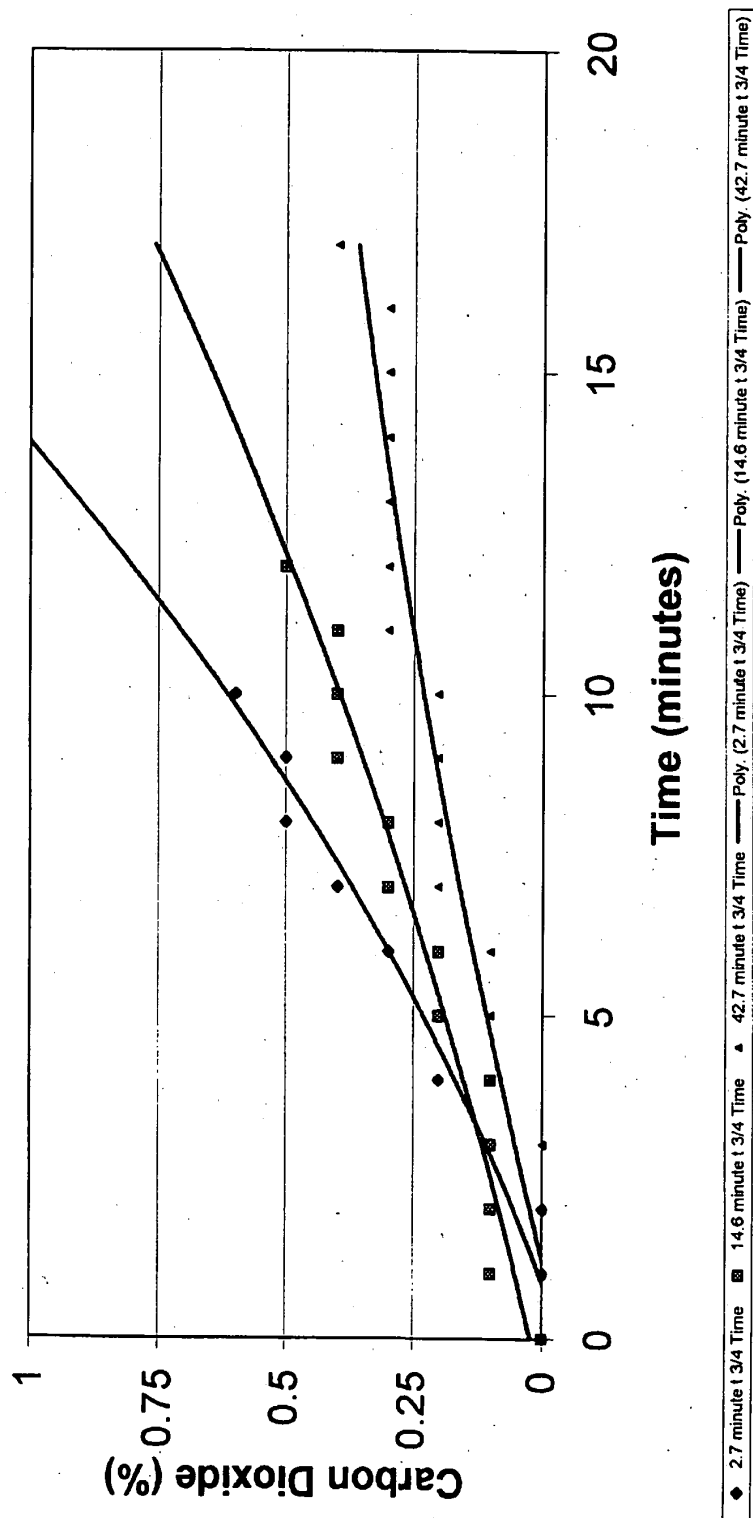


Comparison Between Peak Carbon Dioxide Concentration in Off-Gas with Peak Glyphosate Concentration in Reactor Liquid

FIG. 1



**Carbon Dioxide Evolution Data for Catalytic
Materials with Various $t_{3/4}$ Times
FIG. 2**



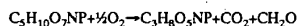
METHOD FOR THE MANUFACTURE OF N-PHOSPHONOMETHYLGLYCINE FROM N-PHOSPHONOMETHYLIMINODIACETIC ACID USING A CATALYTIC CARBON

FIELD OF INVENTION

The present invention relates the use of a catalytically active carbonaceous char for the manufacture of N-phosphonomethylglycine from N-phosphonomethyliminodiacetic acid in the presence of a molecular oxygen containing gas.

BACKGROUND OF THE INVENTION

The use of activated carbon as a catalyst to promote the formation of glyphosate by oxidation of N-phosphonomethyliminodiacetic acid is described by Hershman, U.S. Pat. No. 3,969,398, where N-phosphonomethyliminodiacetic acid is prepared by reacting iminodiacetic acid with formaldehyde and phosphoric acid. Hershman reports teaching that glyphosate is produced by the oxidation of N-phosphonomethyliminodiacetic acid in the presence of activated carbon as a catalyst according to the following proposed reaction:



Rogers et al., U.S. Pat. No. 5,578,190 describes the use of carbon impregnated with various metals. The impregnated carbon is utilized to facilitate a hydrogenation reaction to produce glyphosate.

Cullen et al., International Publication Number WO 96/38455, describes the oxidation of N-phosphonomethyliminodiacetic acid with an oxidizing agent such as hydrogen peroxide in the presence of activated carbon as a catalyst. The oxidation reaction results in the production of glyphosate.

Chou, U.S. Pat. No. 4,624,937, describes the process for modifying an activated carbon capable of oxidizing tertiary amines and secondary amines in the presence of activated carbon. The process describes the modification of the activated carbon by an oxygen-containing gas and ammonia at temperatures from 800° to 1200° C. The modification process enhances the ability of the activated carbon to facilitate the oxidation of the tertiary or secondary amines.

All of the prior art for improving the production of glyphosate from N-phosphonomethyliminodiacetic acid has certain disadvantages, which make the process unattractive from a commercial standpoint. Chief among these is an inability to determine in a rapid and convenient manner the suitability of a char for such applications prior to its use, in particular the intrinsic catalytic activity of the char for glyphosate manufacture. As a result of this shortcoming, it is not possible to know or even to estimate during the preparation of a char the utility of the final product short of actual testing in the application itself.

Accordingly, it is the object of the present invention to provide an improved process for the manufacture of N-phosphonomethylglycine from N-phosphonomethyliminodiacetic acid in the presence of a gas containing molecular oxygen, such as pure oxygen, by contacting said acid with a low temperature catalytically active carbonaceous char in which the intrinsic catalytic activity of the char is measured and known prior to use. It is further the object of the present invention to estimate the intrinsic catalytic activity of the char using a test which is relatively cheap, quick, and simple in its execution and fairly indicative of the suitability of the char for the intended application.

SUMMARY OF THE INVENTION

In general, the present invention comprises an improved process for the manufacture of N-phosphonomethylglycine from N-phosphonomethyliminodiacetic acid in the presence of a molecular oxygen containing gas such as pure oxygen by contacting said media with a carbonaceous char in which the intrinsic catalytic activity of the char is measured and known prior to use. The improvement is in the use of a low temperature catalytically active carbonaceous char, which can rapidly decompose hydrogen peroxide in aqueous solution. More specifically, the carbonaceous char is preferably the low temperature char described in U.S. patent application Ser. No. 09/079,424 [attorney docket 98032] filed May 14, 1998, incorporated herein by reference. Surprisingly, when tested under conditions wherein those char properties known to affect mass transport and adsorption capacity, e.g. under conditions of nearly equivalent apparent density and iodine number, the rate at which the char can decompose hydrogen peroxide has been found to provide an indication of the utility of the char for the manufacture of glyphosate from N-phosphonomethyliminodiacetic acid. The rate of hydrogen peroxide decomposition is measured by the test described in Example 1 U.S. Pat. No. 5,470,748 Incorporated herein by reference and is reported, except where noted, as the t-¼ time, measured in minutes.

In the present invention it is found that chars having the highest utility for glyphosate manufacture are those having t-¼ times of 15 minutes or less, preferably 10 minutes or less.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graphical representation of the carbon dioxide concentration in the off-gas and the glyphosate in the reactor liquid.

FIG. 2 is a graphical representation of the rate of phosphonomethyliminodiacetic acid oxidation as measured by carbon dioxide evolution as a function of time for three carbons having t-¼ time values of 2.7, 14.6, and 42.7 minutes respectively.

PRESENTLY PREFERRED EMBODIMENTS

The utility of the invention is demonstrated in the following two examples. Example 1 demonstrates the correlation between the carbon dioxide concentration in the reactor off-gas and the glyphosate concentration in the reactor liquid. Example 2 demonstrates the effect of catalytic activity as measured by t-¼ time at pH 7 on the rate of carbon dioxide production in the reactor off-gas which correlates to the glyphosate concentration of the reactor liquid.

EXAMPLE 1

A sample of catalytically active material was sized so that 95% of the particles passed through a 325 mesh Tyler screen. A 0.2 gram sample of the pulverized carbon was added to the stainless steel reactor vessel of the Autoclave Engineers Eze-Seal™ Autoclave. A 0.5 gram aliquot of N-phosphonomethyliminodiacetic acid was added to the reaction flask along with 95 milliliters of deionized water. The stainless steel reactor was connected to the autoclave, and the slurry stirred at 200 rpm under a nitrogen blanket. The slurry was heated externally to 70° C. The slurry was allowed to equilibrate for approximately two hours prior to initiation of the oxidation reaction. After reaching 20 equilibrium, pure oxygen was introduced to the reactor flask at a pressure of 60 psi. The off-gas from the reactor flask was

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monitored using a Nova Model 7550P7 Multi-Gas Analyzer. Liquid samples were periodically withdrawn from the reactor vessel through a sample port and analyzed for glyphosate concentration through the use of a Waters HPLC. The peak carbon dioxide concentration occurred after 18 minutes while the peak glyphosate concentration occurred at 20 minutes. A plot depicting the carbon dioxide concentration in the off-gas and the glyphosate in the reactor liquid is shown in FIG. 1.

EXAMPLE 2

Three catalytically active materials with similar properties other than catalytic activity as measured by the $t_{1/4}$ time at pH 12 were tested using identical conditions to the material in Example 1. Carbon dioxide concentration in the off-gas was analyzed. Data show the rate of carbon dioxide generation was greatest for the catalytically active material with the highest catalytic activity as measured by the $t_{1/4}$ time, while the least catalytically active material had the slowest carbon dioxide generation rate. Data is shown in TABLE 1 below.

TABLE 1

Sample	Iodine Number (mg/g)	Apparent Density (g/cc)	$t_{1/4}$ Time (minutes)
Catalytically Active	1075	0.53	2.7
Catalytically Active	1066	0.53	14.6
Activated Carbon	1066	0.53	42.7

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While a presently preferred embodiment of the invention has been described in particularity, it may be otherwise embodied within the scope of the appended claims.

What is claimed is:

1. The process for the production of N-phosphonomethyl glycine (glyphosphate) which comprises contacting an aqueous solution of N-phosphonomethyliminodiacetic acid with a gas containing molecular oxygen at an elevated temperature to initiate and sustain a reaction in the presence of a low temperature catalytically active carbonaceous char having a $t_{1/4}$ time less than about 15 minutes.

2. The process of claim 1 wherein the $t_{1/4}$ time of said catalytically active carbonaceous char is less than about 10 minutes.

3. The process of claim 1 wherein the $t_{1/4}$ time of said catalytically active carbonaceous char is less than about 5 minutes.

4. The process of claim 1 wherein said catalytically active carbonaceous char is granular, pelleted, shaped, or powdered.

5. The process of claim 1 wherein said catalytically active carbonaceous is formed, bonded, or otherwise incorporated into a unitized body for use as a filtration media.

6. The process of claim 1 wherein said catalytically active carbonaceous char is a fiber, fabric, or cloth.

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United States Patent [19]

Felthouse

[11] Patent Number: 4,582,650

[45] Date of Patent: Apr. 15, 1986

[54] OXIDATION WITH ENCAPSULATED CO-CATALYST

[75] Inventor: Timothy R. Felthouse, St. Louis, Mo.

[73] Assignee: Monsanto Company, St. Louis, Mo.

[21] Appl. No.: 700,170

[22] Filed: Feb. 11, 1985

[51] Int. Cl.⁴ C07F 9/38

[52] U.S. Cl. 260/502.5 F; 423/437;
502/74

[58] Field of Search 260/502.5 F; 423/437,
423/580

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Primary Examiner—J. E. Evans

Attorney, Agent, or Firm—Joseph D. Kennedy; James W. Williams, Jr.

[57] ABSTRACT

Processes are given for which a microcrystalline support having a noble metal located within its pores, is used as a permselective catalyst to oxidize formaldehyde and similar materials while avoiding poisoning by N-phosphonomethylamines. The permselective catalyst can be used as a co-catalyst with activated carbons in the oxidation of N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine.

11 Claims, No Drawings

OXIDATION WITH ENCAPSULATED CO-CATALYST

The present invention relates to methods for catalyzed oxidation of formaldehyde in the presence of N-phosphonomethylglycine, as in methods of preparing N-phosphonomethylglycine by oxidative cleavage of N-phosphonomethyliminodiacetic acid with concurrent oxidation of the formaldehyde side product produced in the reaction, and to catalysts useful in such reactions. In particular, the invention concerns the use of noble metal-microcrystalline support catalysts, in which the noble metal is located within the pores of the support, along with carbon catalysts in such reactions; and the preparation of such catalysts in which the noble metal is relatively inaccessible to poisoning by N-phosphonomethylglycine.

BACKGROUND OF THE INVENTION

One of the most prominent of present day herbicides is N-phosphonomethylglycine or its derivatives. The N-phosphonomethylglycine compound can be prepared by the oxidation of N-phosphonomethyliminodiacetic acid, employing activated carbon as the catalyst, as described in U.S. Pat. No. 3,969,398. In such oxidation, one of the by-products is formaldehyde, and formaldehyde has some tendency to react with and methylate amino compounds, including the desired N-phosphonomethylglycine. Zeolites and synthetic zeolites are known materials which have been employed in various ways as catalysts and catalyst support materials. U.S. Pat. No. 4,299,686 asserts methods of preparing zeolite Alpha containing platinum group metal within the pores and its use in processes requiring shape selectivity for straight-chain compounds for selectoforming, hydrodewaxing, selective cracking, etc. U.S. Pat. No. 3,373,109 refers to having a minor part of metal dispersed within the pores of a crystalline aluminosilicate, and for example, describe materials having channels which permit adsorption and pore diffusion of normal paraffins and olefins having a molecular size smaller than 5 angstroms, and refer to selective high activity restricted to those molecules which do not exceed a maximum critical diameter.

SUMMARY OF THE INVENTION

The invention involves a process for catalyzed oxidation of formaldehyde or formic acid in the presence of N-phosphonomethylglycine, utilizing a noble metal catalyst which is located within the pores of zeolite or other microcrystalline support, in order to avoid or impede contact by the N-phosphonomethylglycine or other process impurities while permitting contact by the formaldehyde. The invention is particularly concerned with effecting such oxidation of formaldehyde during the production of N-phosphonomethylglycine by carbon-catalyzed oxidative cleavage of N-phosphonomethyliminodiacetic acid, as formaldehyde is a by-product in the cleavage reaction and may further react with the desired N-phosphonomethylglycine product.

The invention is further concerned with use of the referred-to noble catalyst in a microporous support, possibly in the presence of activated carbon catalyst, to treat effluent from reactions to produce N-phosphonomethylglycine, to remove formaldehyde therefrom; such effluent may contain amounts of N-phosphonomethylglycine, N-phosphonomethyliminodia-

cetic acid, or other phosphonomethylamines or amino compounds, or reaction impurities. The invention is further concerned with combination catalysts, comprising an activated carbon catalyst and a catalyst comprised of a noble metal dispersed within the pore structure of a microporous support.

DETAILED DESCRIPTION

The present invention involves the use of noble metal catalysts in which the metal is protected from poisoning by being embedded within the pores of a microporous support. The nature of the support and the location of the metal therein is such as to make the metal relatively inaccessible to poisons, thereby extending the life of the catalyst. Ideally, the support will have pores such that the poison is too bulky to penetrate to the metal in the pores, while formaldehyde or other species to be reacted can readily reach the metal. Aside from selectivity based strictly upon size, surface effects can be involved, and particular surface groups can inhibit entry by a compound, even though the compound may appear to be of sufficiently small size to penetrate the pores. The noble metal catalyst materials for use herein have the noble metal located within the pores of a microporous support material, as determined by transmission electron microscopy. Such catalyst materials are referred to herein as encapsulated, although recognizing that the microporous nature of the support provides some openings for penetration. The size of the openings has a significant relationship to penetrability of the support, but large-pore zeolites can be used herein, referring to those with 12 or so ring members. Many of the useful zeolites have 8-10 or fewer ring members, and may, for example, have pore openings of 5 Å. In general, a small molecule such as formaldehyde readily penetrates zeolites, so most of the available zeolite pore sizes are suitable, so far as formaldehyde permeation is concerned. However, difficulties may be encountered in incorporating a noble metal into the channels of some of the very small-pore zeolites. The noble metals will typically be in the form of very small crystallites or particles in order to fit within the voids of the support, such as in the range of about 10 to 20 Å, but larger or smaller particles can be present. However, a substantial amount of the metal crystallites should have diameters no greater than 20 Å, in order to be relatively inaccessible to contact by large molecules. If crystallites of such size are present, they will typically be located within the pores and provide permselective catalytic properties, even though metal crystallites of substantially larger size are also present. The larger size crystallites will be subject to poisoning by such compounds as N-phosphonomethylamines, making the metal in such form relatively ineffective for desired uses, but the accompanying embedded crystallites of less than 20 Å diameter can still have the desired effect.

The present noble metal catalyst materials are designed for semipermeability, i.e., to permit permeation or penetration by species to be oxidized, while hindering penetration by catalyst poisons, such as N-phosphonomethylglycine. With some types of support materials, it may be feasible to have almost complete exclusion of permeation to the metal by the N-phosphonomethylglycine. With other support materials where there is some penetration by the poison, there can still be advantage if the rate of penetration of the formaldehyde or formic acid reactant is many times greater than that of the N-phosphonomethylglycine poison. Since form-

tion under the reaction conditions. Illustrative of other solvents or liquids which can be used are nitriles such as acetonitrile, propionitrile, etc.; nitrocompounds such as nitromethane, and halogenated compounds such as methylene chloride.

The microcrystalline supports used herein are three-dimensional aluminosilicates, zeolites, and it is advisable to select such materials so as to have sufficient acid stability as not to undergo excessive degradation (compositional and/or crystallinity changes) under the conditions of employment, such as in the presence of $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{NR}^1\text{R}^2$, where R^1 and R^2 are organic groups or hydrogen, in aqueous solution at elevated temperatures. Aluminosilicates with an Si/Al ratio of about 2 or more will generally have sufficient acid stability. Examples of zeolites which can be used include mordenite, zeolite Y, zeolite L, zeolite Ω , erionite, ferrierite, offretite, Silicalite, ZSM-5, etc. Additionally various two-dimensional layered materials can be used of the type $\text{Zr}(\text{O}_3\text{PR})_2$, where R includes $-\text{OH}$, $-\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$.

Encapsulation methods for noble metal crystallites comprise a series of steps, in particular sequence in order for the final catalyst to possess the distribution of crystallites residing entirely within the internal pore structure of the microcrystalline support. Three general methods are employed to incorporate the precursor complex within the support. The precursor complexes are selected from either various cationic metal amine species such as $\text{Pt}(\text{NH}_3)_4^{2+}$, $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$, $\text{Pd}(\text{NH}_3)_4^{2+}$, or $\text{Ru}(\text{NH}_3)_6^{3+}$ or suitable organometallic compounds including $\text{Pt}(\text{allyl})_2$, $\text{Pt}(1,5\text{-cyclooctadiene})_2$, $\text{Pt}(\text{ethylene})_3$, $\text{Rh}(\text{allyl})_3$, $\text{Ir}(\text{allyl})_3$, or $\text{Pd}(\text{allyl})_2$.

METHOD 1

A dilute ($<0.1\text{M}$) aqueous solution of the precursor compound exemplified by $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ is stirred with a slurry of the microcrystalline support (particle size typically less than 200 mesh) at room temperature or higher to effect an ion exchange between $\text{Pt}(\text{NH}_3)_4^{2+}$ and zeolite counterions such as NH_4^+ or Na^+ to the extent that $\text{Pt}(\text{NH}_3)_4^{2+}$ is incorporated within the support to ~ 0.1 to ~ 5.0 wt.% as Pt metal. Suitable supports for treatment by this ion-exchange method include the NH_4^+ or Na^+ forms of mordenite, zeolite Y, zeolite L, zeolite Ω (omega), and ZSM-5, although other monocations or mixtures of monocations in the zeolite may be used.

After an appropriate length of time, the $\text{Pt}(\text{NH}_3)_4^{2+}$ /zeolite material is filtered and washed with water until no chloride counterion is detected in the filtrate. The solid catalyst precursor material is then dried in a vacuum oven at $50^\circ\text{--}100^\circ\text{C}$. overnight then sieved to an appropriate particle size, typically below 200 mesh.

Preparation of the encapsulated catalyst from the $\text{Pt}(\text{NH}_3)_4^{2+}$ /zeolite precursor material is accomplished in a flow reactor with the solid located between quartz wool plugs. The solid precursor may be diluted with inert particles of low-surface area alumina or silica of typically 8–14 mesh to lower the pressure drop across the bed and improve gas-solid contacting. After the solid is equilibrated in the reactor under an inert argon gas purge at 100°C ., an atmosphere of O_2/Ar is provided with a total flow rate of the gas blend of 400 ml/min. with 80 ml/min. of O_2 and 320 ml/min. of Ar. The reactor furnace temperature is then increased at a

rate of between $0.2^\circ/\text{min.}$ and $10^\circ/\text{min.}$ up to at least 350°C . and as high as 600°C . in certain instances. The O_2 flow is then stopped after reaching the desired temperature and Ar-purged for at least 3 hr. while cooling the reactor to 300°C . Then a flow of H_2 at 80 ml/min. is introduced into the Ar stream and maintained for 2–3 hr. The reactor is then cooled to 100°C . under an Ar purge of less than 320 ml/min. The above procedure serves to decompose the Pt-amine complex and results in the encapsulation of small Pt crystallites within the internal zeolite pore structure.

The Pt dispersion and particle sizes are evaluated by means of transmission electron microscopy (TEM). Ultramicrotomed thin (100 Å) sections of the Pt/zeolite particles embedded in an epoxy matrix provide the best means of examination. Metal particle sizes must be less than the diameter of the largest void space within the zeolite microstructure in order to be considered "encapsulated". Typically, the metal particles are no greater than 20 Å in size.

METHOD 2

Alternatively, the zeolites described in Method 1 must be used in the NH_4^+ form and calcined in a flow reactor in O_2/Ar at 550°C . for 3 hr. or more. The anhydrous zeolite is then removed from the reactor and suspended in a predried hydrocarbon solvent such as hexane or toluene.

The metal is then introduced as a hydrocarbon-soluble complex [(e.g., $\text{Pt}(\text{allyl})_2$, $\text{Pt}(1,5\text{-cyclooctadiene})_2$, $\text{Pt}(\text{ethylene})_3$, $\text{Rh}(\text{allyl})_3$, $\text{Ir}(\text{allyl})_3$, or $\text{Pd}(\text{allyl})_2$] containing at least one ligand subject to elimination when contacted with the hydrocarbon slurry of the anhydrous zeolite. After stirring under a dry atmosphere for two or more days, the zeolite slurry is filtered then rinsed well with the hydrocarbon solvent. After drying at room temperature and under vacuum, the zeolite containing the adsorbed oxide-bound metal complex is treated under a H_2 or inert gas atmosphere in a flow reactor at $25^\circ\text{--}200^\circ\text{C}$. for a length of time necessary to decompose the complex. The catalyst so prepared may be evaluated via TEM as described in Method 1.

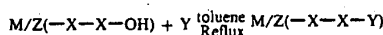
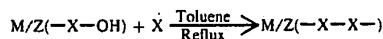
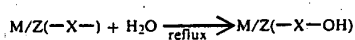
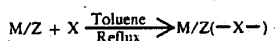
METHOD 3

For acid stable zeolites with pore openings consisting of ten or fewer Si and/or Al and oxygen atoms (ten member rings or less) or pore openings less than 6.5 Å it is generally necessary to entrap the metal precursor complex directly in the internal zeolite pore structure during the zeolite synthesis. Synthetic zeolites of this type include erionite, ferrierite, offretite, and ZSM-5 or its all-silica analogue, Silicalite. Zeolite syntheses are performed as prescribed in U.S. Pat. Nos. 2,950,952 (Zeolite T or erionite), 3,966,883 (ferrierite), 4,093,699 (offretite), 3,702,886 (ZSM-5), and 4,067,724 (silicalite), except that ~ 0.5 to ~ 2.0 wt.-% as Pt of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ (or other noble metal amine complex) is added to the synthesis mixture.

The $\text{Pt}(\text{NH}_3)_4^{2+}$ /zeolite catalyst precursor material obtained by this direct synthesis procedure is washed free of halide ions then optionally ion-exchanged at least three times with 2.2M NH_4Cl solution. After all halide ions are again rinsed free of the material, it is dried in a vacuum oven at $50^\circ\text{--}100^\circ\text{C}$. and sieved to an appropriate particle size, usually below 200 mesh. The encapsulated noble-metal zeolite composition is then obtained using the activation procedure described in Method 1.

For the encapsulated noble metal catalysts prepared using Method 1, it is desirable to perform the ion exchange of the metal complex cation on the NH_4^+ form of the zeolite in order for the final encapsulated catalyst to contain a high density of surface hydroxyl groups formed from decomposition of the NH_4^+ ions. The pore size and surface characteristics of those encapsulated metal/zeolite catalysts which may need further modification can be modified so as to discriminate between formaldehyde and various larger N-phosphonomethylamines such as $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$ by the techniques outlined below.

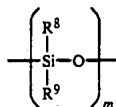
(1) Solution Modification. Various soluble reagents "X" are reacted with a hydrocarbon (e.g., toluene) slurry of the anhydrous metal/zeolite catalyst using some or all of the steps listed below. A list of suitable "X" reagents includes chlorosilane monomers of the form $\text{R}_x^3\text{R}_y^4\text{R}_z^5\text{SiCl}_{4-x-y-z}$ ($0 < x < 3$, $0 < y < 2$, $0 < z < 1$, R^3 methyl, ethyl, propyl, isopropyl, butyl, phenyl, and R^4 and R^5 may also be selected from the list for R^3 in various combinations) and chloro-terminated polydimethylsiloxane oligomers of the form $\text{ClSi}(\text{CH}_3)_2\text{O}-(\text{Si}(\text{CH}_3)_2\text{O})_n-\text{Si}(\text{CH}_3)_2\text{Cl}$ ($n=4, 5, 6$). The metal/zeolite catalyst is denoted as M/Z.



Steps (b) and (d) require vacuum dehydrations after their completion at $150^\circ\text{--}200^\circ\text{C}$. and less than 10^{-3} torr. Reagent Y is selected from various volatile trimethylsilyl-transfer agents such as $(\text{CH}_3)_3\text{SiCl}$ or $(\text{CH}_3)_3\text{SiNH-Si}(\text{CH}_3)_3$.

(2) Vapor-Phase Modification. The encapsulated metal/zeolite catalysts may also be modified by gas-phase reagents at temperatures above the boiling point of the reagent to 600°C . in a flow reactor. Reagents envisioned for use by this method include $(\text{CH}_3)_3\text{SiCl}$, $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$, $\text{Si}(\text{OR}^6)_4$ ($\text{R}^6 = \text{methyl, ethyl}$), and $\text{Ti}(\text{OR}^7)_4$ ($\text{R}^7 = \text{isopropyl, butyl}$).

(3) Catalyst Precursor Modification. Catalyst precursors prepared by means of Method 1 above may be impregnated after drying with various Si- or Ti-containing compounds including $\text{Si}(\text{OR}^6)_4$, $\text{Ti}(\text{OR}^7)_4$, and



where this silicone is of the type described in U.S. Pat. No. 4,402,867 and R^8 and R^9 are individually selected from the group consisting of hydrogen, methyl, fluorine, chlorine, and hydroxy, and m is an integer of at least 3. The impregnated catalyst precursor (e.g., $\text{Pt}(\text{NH}_3)_4^{2+}/\text{zeolite}$) is then dried in a vacuum, sieved to the appropriate particle size, and charged to a flow

reactor. Treatment in O_2/Ar followed by H_2/Ar is identical to the procedure given in Method 1.

Oxidation procedures were conducted in a 300-ml 316 stainless steel "Magnedrive" autoclave from Autoclave Engineers. A continuous flow through the reactor of O_2 at $150\text{--}60\text{ cc/min}$ was used to purge the reactor of the CO_2 by-product. The extent of the oxidation was continuously monitored by the cumulative total of CO_2 in the O_2 off gas and detected using a Wilks Miran II Process Analyzer. Typically, a 2.0 ml charge of 37% formaldehyde solution was added to 98.0 ml of water and the mixture charged along with 0.10 to 0.25 g of catalyst. The N-phosphonomethylamine was added as a solid by means of injection with O_2 pressure into the reactor at the appropriate time without disassembling the autoclave. Formaldehyde could also be added in this fashion. Formaldehyde oxidations in the absence and the presence of the N-phosphonomethylamine were performed at $95 \pm 3^\circ\text{C}$, 30 psig O_2 (206.85 kPa) at the flow rate given above, and 1500 rpm stirring rate.

EXAMPLE 1

A platinum-encapsulated catalyst was prepared by ion exchange of an aqueous slurry of Union Carbide LZM8, NH_4 -mordenite ($\text{NH}_4\text{--MOR}$) in a 0.023M solution of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$. After stirring overnight the slurry was filtered then rinsed by resuspension in water followed by filtration until chloride ion was no longer detected in the filtrate. The $\text{Pt}(\text{NH}_3)_4^{2+}/\text{NH}_4\text{--MOR}$ catalyst precursor was vacuum dried overnight at 80°C . then sieved to below 200 mesh. A mixture of 1.5 g of $\text{Pt}(\text{NH}_3)_4^{2+}/\text{NH}_4\text{--MOR}$ and 7.0 cc of 8×14 mesh Al_2O_3 was charged to a quartz reactor tube and contained with quartz wool plugs. The reactor was equilibrated at 100°C . under $\sim 10\text{ cc/min}$ Ar purge. With a flow of 80 cc/min O_2 and 320 cc/min Ar, the reactor was increased in temperature at $0.2^\circ/\text{min}$. to 350°C . The O_2 flow was then discontinued as the reactor was cooled to 300°C . After 3 hr. a flow of 80 cc/min H_2 was introduced into the 320 cc/min . gas stream for a 2 hr. period. The reactor was then cooled to 100°C . The 3.30% Pt/H-MOR catalyst so treated was recovered and found to have no Pt crystallites in excess of 20 \AA as seen from transmission electron microscopy.

The catalyst was evaluated in the 300-ml autoclave for formaldehyde oxidation as previously described and as summarized in Table 1. By comparison, a catalyst that is not encapsulated shows little formaldehyde oxidation activity once contacted with N-phosphonomethylglycine (see Table II). Additionally, as can be seen in the reaction data displayed between formaldehyde charges 10 and 14 in Table I these encapsulated catalysts differ from conventional supported noble metal catalysts (Pt/C) in that they can be washed free of adsorbed poisons (glyphosate) and this simple regenerative procedure restores the initial activity (charges 2 and 3 in Table I).

Mesh sizes given in Example 1 or elsewhere in the specification are those of the U.S. Standard Sieve Series.

TABLE I

Autoclave Evaluation Data for 3.30% Pt/H-MOR ^a for Formaldehyde Oxidation in the Absence and Presence of N-Phosphonomethylglycine		
Formaldehyde Charge No.	Reaction Time, Min.	Formaldehyde Conversion, %
1	51	87.3

TABLE I-continued

Autoclave Evaluation Data for 3.30% Pt/H—MOR ^a for Formaldehyde Oxidation in the Absence and Presence of N—Phosphonomethylglycine		
Formaldehyde Charge No.	Reaction Time, Min.	Formaldehyde Conversion, %
2 ^b	24	100.0
3 ^c	21	100.0
4	54	100.0
5	45	100.0
6	54	100.0
7 ^d	36	100.0
8	39	100.0
9 ^e	117	96.9
10	48	45.9
11 ^f	30	100.0
12	27	100.0
13	27	100.0
14 ^g	45	100.0
15	60	96.5
16	27	2.55
17 ^f	78	100.0
18	45	100.0
19	45	100.0
20 ^g	117	90.3
21	33	8.49

^aInitial autoclave charge: 0.10 g. Platinum loading determined by elemental analysis.^bTotal catalyst charge is now 0.25 g.^cAdded 0.20 g of N—phosphonomethylglycine^dAdded another 0.20 g of N—phosphonomethylglycine; total charge: 0.40 g.^eResidual catalyst activity after stirring ~65 hr. in a solution of 0.40 g of N—phosphonomethylglycine.^fCatalyst filtered off, rinsed with water, and returned to the autoclave.

TABLE II

Autoclave Evaluation Data for ~2% Pt/CPG ^a for Formaldehyde Oxidation in the Absence and Presence of N—Phosphonomethylglycine		
Formaldehyde Charge Number	Reaction Time, Min.	Formaldehyde Conversion, %
1	21	100.0
2	21	100.0
3	21	100.0
4 ^b	37	9.3

^aCatalyst prepared with 100% controlled pore glass (CPG) of 200–400 mesh by incipient wetness method with aqueous Pt(NH₃)₃(NO₃)₂. Catalyst charge: 0.25 g.^bAdded 0.30 g of N—phosphonomethylglycine.

EXAMPLE 2

Some platinum-encapsulated catalysts require further functionalization in order to tailor the pore size and surface adsorption sites selectively to entry of formaldehyde into the internal pore structure in the presence of N-phosphonomethylglycine in the bulk solution. To illustrate this point a sample of Union Carbide NaY(L-ZY72) was thoroughly exchanged three times with 2.2M NH₄Cl solution. The NH₄Y zeolite was then exchanged with a 0.015M solution of Pt(NH₃)₄Cl₂. The Pt(NH₃)₄²⁺/NH₄Y precursor catalyst was dried in a vacuum oven at 80° C. overnight then sieved to below 200 mesh. The precursor catalyst was then charged to a quartz flow reactor between quartz wool plugs, purged with Ar at 100° C., and treated with O₂/Ar while the furnace temperature was ramped to 600° C. The thermal ramping rate was 2°/min. to 250° C. then 0.5°/min. up to 600° C. After 3-hr. purge in Ar while the reactor cooled to 300° C., an H₂/Ar gas mixture was passed through the catalyst bed for 2 hr. The reactor was cooled to 100° C. in an Ar gas purge.

The catalyst prepared by the above method showed significant poisoning within the time that two charges of formaldehyde were added in sequence. The results are shown in Table III.

TABLE III

Autoclave Evaluation Data for ~3% Pt/HY ^a for Formaldehyde Oxidation in Absence and Presence of N—Phosphonomethylglycine		
Formaldehyde Charge Number	Reaction Time, Min.	Formaldehyde Conversion, %
1	18	100.0
2	18	100.0
3	18	100.0
4 ^b	42	100.0
5	42	47.5

^aCatalyst charge: 0.10 g.^bAdded 0.20 g of N—phosphonomethylglycine.

In contrast, surface modification of the ~3% Pt/HY using chlorine-terminated polydimethylsiloxane (Cl—PDMSi—Cl, Petrarch Systems PS375) extended the number of formaldehyde oxidation cycles completed once N-phosphonomethylglycine was added. The Pt/HY catalyst was prepared using an identical procedure to the catalyst in Table III. However, after oxidation in O₂/Ar followed by reduction in H₂/Ar, the catalyst was recovered in an N₂-containing drybox. The catalyst powder was then treated with an excess of Cl—PDMSi—Cl, diluted with dry toluene, and refluxed overnight as a suspension in toluene. The treated catalyst designated ~3% Pt/HY(—PDMSi—) was filtered in air, washed with hexanes, and dried in a vacuum oven at 115° C. overnight. A sample of this catalyst gave the results shown in Table IV.

TABLE IV

Autoclave Evaluation Data for ~3% Pt/HY(—PDMSi—) ^a for Formaldehyde Oxidation in the Absence and Presence of N—Phosphonomethylglycine		
Formaldehyde Charge Number	Reaction Time, Min.	Formaldehyde Conversion, %
1	21	100.0
2 ^b	18	100.0
3	21	100.0
4	21	100.0
5 ^c	21	100.0
6	21	100.0
7 ^b	48	100.0
8	54	63.7

^aCatalyst charge: 0.15 g.^bAdded 0.20 g of N—phosphonomethylglycine.^cCatalyst filtered off, rinsed with water, and returned to autoclave.

The surface modified catalyst shown in Table IV extends the poisoning resistance by 2–3 cycles over the catalyst in Table III.

A co-catalyst as described herein can be usefully employed in processes to convert N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine under conditions in general effective for such conversion, including those taught in the referred-to U.S. Pat. No. 3,969,398. Thus the conversion can be carried out under conditions described in the following example.

EXAMPLE 3

To a 300 ml. autoclave as described above 100 ml. deionized water, 1 gram of Norit A activated carbon, and 4 grams N-phosphonomethyliminodiacetic acid are charged. There is also added a 0.15 gram amount of the 3.30% Pt/H—MOR catalyst of Example 1. The contents are heated to 90° C. with oxygen flowing at atmospheric pressure. The contents are heated to about 95° C. with agitation for approximately two hours, with yields of N-phosphonomethylglycine in excess of 95% expected to be obtainable. Because of the effectiveness of the noble metal catalyst in oxidizing the formaldehyde, the moles of CO₂ generated may be expected to

approach 1.9 or so for each mole of reactant, with the amount of formaldehyde remaining being less than 10% of theoretical and in concentrations possibly around 0.1% or lower by weight. Thus the tendency of formaldehyde to react with the N-phosphonomethylglycine product will be markedly diminished.

While the present encapsulated catalysts are of particular interest for oxidation of formaldehyde in the presence of N-phosphonomethylglycine or other products of oxidative cleavage reactions of N-phosphonomethylaminodiacetic acid or other glycine derivatives, the catalysts will also be useful for oxidation in the presence of other catalyst poisons having size and zeolite diffu-

sive oxidation of formaldehyde under practical conditions in the presence of such poison, in a reasonable time period, such as half-an-hour to an hour or so. Ethylenediaminetetraacetic acid, quinaline and 4-methylquinoline are examples of nitrogen bases against which encapsulated catalysts can provide protection in accord with the present invention.

A number of catalysts were prepared in accord with procedures described herein, and their characterization by transmission electron microscopy is reported in Table V, along with that of a platinum on silica catalyst. The catalyst description includes the percentage of platinum in the catalyst.

TABLE V

Summary of Platinum Catalysts and Their Characterization by Transmission Electron Microscopy

Catalyst Description	Catalyst Support Particle Size ^a (μm)	TEM Data ^b	
		Pt Particle Sizes	Å Distribution ^c
1.79% Pt/SiO ₂	74-595 ^d	15-40	M
2.90% Pt/HY	1.47	10-20	M
3.23% Pt/HY(-PDMSi-) ^e	1.48	10-15	M
3.30% Pt/H-MOR	1.06	9-18	M
3.57% Pt/H-MOR	1.06	9-18	M
2.62% Pt/H-ZSM-5	5.90	10-15	M
3.54% Pt/H-ZSM-5	5.54	10-20	C
0.38% Pt/H-ZSM-5	5.54	13-40	C
3.1% Pt/H-ZSM-5	—	15-44	C
		75-200	

^aParticle size determined from Coulter Counter measurements and reported as the average value unless otherwise noted.

^bSpecimens were in most cases (100 keV) ultramicrotomed sections of the catalyst embedded in epoxy resin.

^cCodes for the observed metal dispersions: M = monomodal, C = continuous range of particle sizes.

^dParticle size range for microspheroidal silica, Grace Grade 56.

^ePDMSi = polydimethylsiloxane oligomer attached to the zeolite surface by the reaction between the reduced Pt/HY sample (surface silica hydroxyl groups) and chlorine-terminated PDMSi in dry toluene.

^fParticle size not determined.

sion characteristics like those of N-phosphonomethylglycine. Various amines and other nitrogen bases are capable of poisoning the noble metal oxidation catalysts, and encapsulation in porous carriers as taught herein is effective in avoiding or inhibiting such poisoning in a number of cases, particularly when the poison is a relatively large molecule, such as of molecular weight over 100, or even over 150. Even if poisoning is not avoided, the encapsulated catalyst may still show some improvement in activity and life over a catalyst in which the active metal has not been protected. The value of various degrees of improvement may depend upon the particular application. However, it is apparent that an encapsulated catalyst can be considered effectively protected against a particular poison in a formaldehyde oxidation, if it makes possible nearly quantita-

The effect of various nitrogen bases on formaldehyde oxidation with various platinum catalyst was determined and reported in Table VI below. All experiments were conducted in a 300-mL Autoclave Engineers Magnedrive autoclave run at 1500 rpm at a temperature of 95° C. and 30 psig O₂. A continuous flow of O₂ (mixed with CO₂ product) at 150-60 cm/min. afforded a means to monitor the conversion of the formaldehyde substrate with a calibrated Wilks Miran II Process Analyzer (IR detector). Typically 2.0 mL of 37% formaldehyde solution, 100-mL of water, and 0.10 to 0.50 g of catalyst was charged to the autoclave. Except where noted, 3.4 × 10⁻⁴ moles of nitrogen base were charged to the reactor. All Pt/zeolite samples used were in the "Pt-encapsulated" form. H₄EDTA = Ethylenediaminetetraacetic acid.

TABLE VI

Summary of the Effect of Various Nitrogen Bases on the Formaldehyde Oxidation Endpoint with Various Platinum Catalysts

Catalyst	No Base Conversion (min.)	Endpoint (min.) with Nitrogen Base (% Conversion)				
		Glycine	H ₄ EDTA	Pyridine	Quinoline	4-methylquinoline
1.79% Pt/SiO ₂	45	60(5.2)	60(57.5)	39(6.7)	60(16.7)	—
2.93% Pt/HY	18	60(15.4)	60(52.8)	—	—	—
3.23% Pt/HY(-PDMSi-)	16	60(17.9)	15(100)	—	—	—
			18(100) ^a	—	—	—
			27(99.6)	—	—	—
			60(64.4)	—	—	—
3.5% Pt/H-MOR	20	60(55.5)	21(100)	60(89.2)	24(100)	—
			21(100)	60(74.2)	24(100)	—
			21(100)	—	24(100)	—
			—	—	21(100)	—
3.54% Pt/H-ZSM-5	20	60(75.1)	27(100)	60(20.3)	60(40.9)	18(100)

TABLE VI-continued

Summary of the Effect of Various Nitrogen Bases on the Formaldehyde Oxidation Endpoint with Various Platinum Catalysts						
Catalyst	No Base 100% Conversion (min.)	Endpoint (min.) with Nitrogen Base (% Conversion)				
		Glycine	H ₄ EDTA	Pyridine	Quinoline	4-methyl- quinoline
		60(78.8)	33(100) 36(99.5)			18(100) 18(100) 18(100)
3.17% Pt/H—ZSM-5	18	—	—	—	—	24(100) 24(100) 24(100) ^b 27(100) 27(100) ^c 45(100) 45(100) 54(100) ^d 54(100)

^aHere and in succeeding experiments, these data represent subsequent formaldehyde cycles with a fresh formaldehyde charge.

^b4-Methylquinoline total charge: 6.8×10^{-4} moles.

^c4-Methylquinoline total charge: 3.4×10^{-3} moles.

^dFormaldehyde oxidation endpoint after 24 hrs. in 0.034 M 4-methylquinoline.

I claim:

1. The method of oxidizing formaldehyde or formic acid in the presence of an N-phosphonomethyl amine which comprises contacting a liquid solution containing formaldehyde or formic acid and an N-phosphonomethylamine with oxygen in the presence of a catalyst comprising a microporous support with a noble metal oxidation catalyst located within the pores of such support, with the support being a microporous acid resistant aluminosilicate having an Si to Al ratio of at least 2 and with the microporous support being selectively permeable so as to inhibit contact of the N-phosphonomethylamine with the noble metal therein, at a temperature sufficiently elevated to effect the desired oxidation.
2. The method of claim 1 in which the formaldehyde or formic acid are produced as by-products in an oxidative cleavage reaction of an N-phosphonomethylamine to produce a different N-phosphonomethylamine compound, with such reaction involving use of an active carbon catalyst.
3. The process of claim 1 in which the aluminosilicate is a zeolite of the mordenite class.
4. The process of claim 1 in which the catalyst is a zeolite containing platinum crystallites within the pores and generally of diameters no greater than 20 Å as measured by transmission electron microscopy.
5. The method of claim 1 in which the noble metal catalyst is used as a co-catalyst along with activated carbon catalyst to effect oxidative cleavage of N-phosphonomethyliminodiacetic acid to N-phosphonome-

thylglycine and concurrent oxidation of the formaldehyde by-product.

6. The method of claim 5 in which the oxidation is conducted at temperatures of 25° to 200° C. and oxygen pressures of 50 to 20,000 kPa.

7. The method of claim 5 in which the oxidation is conducted at temperatures of 75° to 150° C. and pressures of 100 to 700 kPa.

8. The method of claim 1 in which the catalyst has been modified by a chlorosilane compound, a chloro-terminated siloxane oligomer, or a silicone polymer.

9. The method of claim 1 in which the microporous support is a zeolite characterized by pore openings no greater than about 8 Å.

10. The method of claim 1 in which the microporous support is characterized by pore openings no greater than about 5 Å and platinum has been incorporated in the zeolite during its preparation.

11. The method of oxidizing formaldehyde of formic acid with a noble metal catalyst in a waste stream which comprises contacting a waste stream containing formaldehyde or formic acid with oxygen in the presence of a catalyst comprising a microporous support with a noble metal catalyst located within the pores of such support, with the support being a microporous, acid resistant aluminosilicate having an Si to Al ratio of at least 2, and with the waste stream also containing a poison for the noble metal and the microporous support being selectively permeable so as to inhibit contact of the poison with the metal therein.

* * * * *

United States Patent [19]

Felthouse

[11] Patent Number: 4,582,650

[45] Date of Patent: Apr. 15, 1986

[54] OXIDATION WITH ENCAPSULATED CO-CATALYST

[75] Inventor: Timothy R. Felthouse, St. Louis, Mo.

[73] Assignee: Monsanto Company, St. Louis, Mo.

[21] Appl. No.: 700,170

[22] Filed: Feb. 11, 1985

[51] Int. Cl.⁴ C07F 9/38

[52] U.S. Cl. 260/502.5 F; 423/437;
502/74

[58] Field of Search 260/502.5 F; 423/437,
423/580

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3,950,402	4/1976	Franz 260/502.5 F	
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3,969,398	7/1976	Hershman 260/502.5 F	
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Primary Examiner—J. E. Evans

Attorney, Agent, or Firm—Joseph D. Kennedy; James W. Williams, Jr.

[57] ABSTRACT

Processes are given for which a microcrystalline support having a noble metal located within its pores, is used as a permselective catalyst to oxidize formaldehyde and similar materials while avoiding poisoning by N-phosphonomethylamines. The permselective catalyst can be used as a co-catalyst with activated carbons in the oxidation of N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine.

11 Claims, No Drawings

OXIDATION WITH ENCAPSULATED CO-CATALYST

The present invention relates to methods for catalyzed oxidation of formaldehyde in the presence of N-phosphonomethylamines, as in methods of preparing N-phosphonomethylglycine by oxidative cleavage of N-phosphonomethyliminodiacetic acid with concurrent oxidation of the formaldehyde side product produced in the reaction, and to catalysts useful in such reactions. In particular, the invention concerns the use of noble metal-microcrystalline support catalysts, in which the noble metal is located within the pores of the support, along with carbon catalysts in such reactions; and the preparation of such catalysts in which the noble metal is relatively inaccessible to poisoning by N-phosphonomethylamines.

BACKGROUND OF THE INVENTION

One of the most prominent of present day herbicides is N-phosphonomethylglycine or its derivatives. The N-phosphonomethylglycine compound can be prepared by the oxidation of N-phosphonomethyliminodiacetic acid, employing activated carbon as the catalyst, as described in U.S. Pat. No. 3,969,398. In such oxidation, one of the by-products is formaldehyde, and formaldehyde has some tendency to react with and methylate amino compounds, including the desired N-phosphonomethylglycine. Zeolites and synthetic zeolites are known materials which have been employed in various ways as catalysts and catalyst support materials. U.S. Pat. No. 4,299,686 asserts methods of preparing zeolite Alpha containing platinum group metal within the pores and its use in processes requiring shape selectivity for straight-chain compounds for selectoforming, hydrodewaxing, selective cracking, etc. U.S. Pat. No. 3,373,109 refers to having a minor part of metal dispersed within the pores of a crystalline aluminosilicate, and for example, describe materials having channels which permit adsorption and pore diffusion of normal paraffins and olefins having a molecular size smaller than 5 angstroms, and refer to selective high activity restricted to those molecules which do not exceed a maximum critical diameter.

SUMMARY OF THE INVENTION

The invention involves a process for catalyzed oxidation of formaldehyde or formic acid in the presence of N-phosphonomethylglycine, utilizing a noble metal catalyst which is located within the pores of zeolite or other microcrystalline support, in order to avoid or impede contact by the N-phosphonomethylglycine or other process impurities while permitting contact by the formaldehyde. The invention is particularly concerned with effecting such oxidation of formaldehyde during the production of N-phosphonomethylglycine by carbon-catalyzed oxidative cleavage of N-phosphonomethyliminodiacetic acid, as formaldehyde is a by-product in the cleavage reaction and may further react with the desired N-phosphonomethylglycine product.

The invention is further concerned with use of the referred-to noble catalyst in a microporous support, possibly in the presence of activated carbon catalyst, to treat effluent from reactions to produce N-phosphonomethylglycine, to remove formaldehyde therefrom; such effluent may contain amounts of N-phosphonomethylglycine, N-phosphonomethyliminodia-

cetic acid, or other phosphonomethylamines or amino compounds, or reaction impurities. The invention is further concerned with combination catalysts, comprising an activated carbon catalyst and a catalyst comprised of a noble metal dispersed within the pore structure of a microporous support.

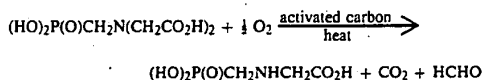
DETAILED DESCRIPTION

The present invention involves the use of noble metal catalysts in which the metal is protected from poisoning by being embedded within the pores of a microporous support. The nature of the support and the location of the metal therein is such as to make the metal relatively inaccessible to poisons, thereby extending the life of the catalyst. Ideally, the support will have pores such that the poison is too bulky to penetrate to the metal in the pores, while formaldehyde or other species to be reacted can readily reach the metal. Aside from selectivity based strictly upon size, surface effects can be involved, and particular surface groups can inhibit entry by a compound, even though the compound may appear to be of sufficiently small size to penetrate the pores. The noble metal catalyst materials for use herein have the noble metal located within the pores of a microporous support material, as determined by transmission electron microscopy. Such catalyst materials are referred to herein as encapsulated, although recognizing that the microporous nature of the support provides some openings for penetration. The size of the openings has a significant relationship to penetrability of the support, but large-pore zeolites can be used herein, referring to those with 12 or so ring members. Many of the useful zeolites have 8-10 or fewer ring members, and may, for example, have pore openings of 5 Å. In general, a small molecule such as formaldehyde readily penetrates zeolites, so most of the available zeolite pore sizes are suitable, so far as formaldehyde permeation is concerned. However, difficulties may be encountered in incorporating a noble metal into the channels of some of the very small-pore zeolites. The noble metals will typically be in the form of very small crystallites or particles in order to fit within the voids of the support, such as in the range of about 10 to 20 Å, but larger or smaller particles can be present. However, a substantial amount of the metal crystallites should have diameters no greater than 20 Å, in order to be relatively inaccessible to contact by large molecules. If crystallites of such size are present, they will typically be located within the pores and provide permselective catalytic properties, even though metal crystallites of substantially larger size are also present. The larger size crystallites will be subject to poisoning by such compounds as N-phosphonomethylamines, making the metal in such form relatively ineffective for desired uses, but the accompanying embedded crystallites of less than 20 Å diameter can still have the desired effect.

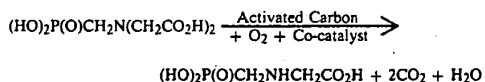
The present noble metal catalyst materials are designed for semipermeability, i.e., to permit permeation or penetration by species to be oxidized, while hindering penetration by catalyst poisons, such as N-phosphonomethylglycine. With some types of support materials, it may be feasible to have almost complete exclusion of permeation to the metal by the N-phosphonomethylglycine. With other support materials where there is some penetration by the poison, there can still be advantage if the rate of penetration of the formaldehyde or formic acid reactant is many times greater than that of the N-phosphonomethylglycine poison. Since form-

aldehyde and formic acid readily penetrate the zeolite materials, a marked hindrance of N-phosphonomethylglycine passage can cause a large difference in rates. In addition to effects of pore size in excluding the larger molecules, diffusion factors may have a significant effect on the penetration rate, particularly in the liquid reaction systems contemplated in the present invention. While penetration rates have not been measured, the rates of formaldehyde may well be several hundred times or more greater than that of N-phosphonomethylglycine. In terms of advantage, it is desirable that the encapsulated noble metal catalyst have two or more times the life of the unencapsulated catalyst, and in fact it may ultimately be feasible for practical operation to have catalyst life many times that of the unencapsulated catalyst and sufficient to make replacement or regeneration of the noble metal catalyst a minor factor in process economics. Moreover, with regard to regeneration, it has been found that the encapsulated catalysts herein are amenable to ready regeneration by simple procedures.

The present invention is particularly concerned with a reaction to prepare N-phosphonomethylglycine by oxidative cleavage of N-phosphonomethyliminodiacetic acid,



The reaction works well, and is a suitable process for preparing N-phosphonomethylglycine. However, the formaldehyde by-product has a tendency to react further with amines, including the desired N-phosphonomethylglycine and other N-phosphonomethylamines, thereby detracting from yield of the desired product. The present invention overcomes this problem by using a co-catalyst along with the carbon, so that the formaldehyde is further oxidized to carbon dioxide and water, thereby becoming unavailable for reaction with the N-phosphonomethylglycine product, as illustrated by the following equation:



In carrying out the reaction, it is important to protect the co-catalyst from ready contact by the N-phosphonomethylamines present, as noble metal crystallite catalysts are quickly poisoned by such compounds. In the illustrated reaction showing formaldehyde as a by-product, some of the formaldehyde may be converted to formic acid which can similarly undergo interfering reactions, and in the present invention the formic acid can also be oxidized to carbon dioxide and water.

The present invention can use various noble metals for the co-catalysts, e.g., Ru, Os, Rh, Ir, Pd and Pt, with Rh or Pt generally being preferred. The amount of noble metal in the microporous support can vary widely, but will generally be in the range of above 0.1% to about 5% by weight, and amounts of about 3% or so are suitable for illustration.

In accordance with an embodiment of this invention, N-phosphonomethyliminodiacetic acid is dissolved in water and this solution contacted with a molecular oxygen-containing gas in the presence of activated car-

bon and a zeolite encapsulated co-catalyst, while heating the mixture to a temperature sufficiently elevated to cause said oxygen and said N-phosphonomethyliminodiacetic acid to react to produce N-phosphonomethylglycine.

The temperature employed in carrying out the oxidation process should be sufficient to initiate the reaction and to sustain the reaction once initiated. Temperatures of from about 25° C., to 150° C. or even higher are usually satisfactory. As those skilled in the art would realize, at lower temperatures the rate of reaction is undesirably slow and, therefore, temperatures of at least 75° C. are preferred and even more preferred are temperatures in the range of about 90° C. to 150° C. It is, of course, realized that at temperatures above about 100° C. that pressure will have to be maintained on the system to maintain a liquid phase.

The pressure at which the process to prepare N-phosphonomethylglycine is conducted can vary over wide ranges. Thus, the pressure of the molecular oxygen-containing gas can be as low as 50 kPa to 20,000 kPa or higher. It is preferred for convenience to conduct the process at a total pressure of from about 50 kPa to 20,000 kPa. It is even more preferred to conduct the process at pressures of from ambient atmospheric pressure to 700 kPa.

The manner in which the aqueous solution of the N-phosphonomethyliminodiacetic acid is contacted with the molecular oxygen-containing gas and activated carbon and co-catalyst can vary greatly. For example, the N-phosphonomethyliminodiacetic acid solution can be placed in a closed container with some free space containing molecular oxygen and shaken vigorously or agitated by stirring or the molecular oxygen-containing gas can be bubbled through said solution containing activated carbon and co-catalyst either through a straight tube or a tube with a fritted diffuser attached thereto. The contacting can also be accomplished in a tubular continuous reactor packed with activated carbon and co-catalyst. Thus, the process of this invention only requires actively contacting the molecular oxygen containing gas with the aqueous solution of said N-phosphonomethyliminodiacetic acid containing said activated carbon catalyst and co-catalyst.

In conducting the oxidation process it is often preferred to employ approximately saturated solutions of the N-phosphonomethyliminodiacetic acid in water at the temperature of reaction for ease of reaction and ease of recovery of the product, N-phosphonomethylglycine, i.e., from about 1% by weight at 25° C., about 4% by weight at 95° C. It is, of course, possible to employ very dilute, i.e., 0.1% by weight of N-phosphonomethyliminodiacetic acid in water; however, this results in a more difficult product recovery procedure.

The reaction, of course, occurs in the aqueous phase when the solution comes in contact with the presence of the catalyst. Thus it is possible to use supersaturated solutions or slurries in which the reactant removed from solution by the oxidation reaction is replaced by the dissolution of more reactant. This maintains the amount of available reactant at a maximum and is therefore preferred to operating in a highly dilute solution.

The amount of the molecular oxygen-containing gas employed can vary over wide ranges. It is, of course, obvious to those skilled in the art that the best yields of the N-phosphonomethylglycine are produced when at least stoichiometric amounts of oxygen are employed.

In most instances for ease of reaction and best yields of the final product, N-phosphonomethylglycine, the amount of oxygen employed would ordinarily be at least $\frac{1}{2}$ mole of oxygen for each mole of N-phosphonomethyliminodiacetic acid employed. In actual practice, the amount of oxygen employed will be from $\frac{1}{2}$ to 1 or more moles for each mole of the N-phosphonomethyliminodiacetic acid employed since the efficiency of the oxygen utilization is usually less than 100%.

By the term "molecular oxygen-containing gas", as employed herein, is meant any gaseous mixture containing molecular oxygen with one or more diluents which are non-reactive with the oxygen or with the reactant or product under the conditions of reaction. Examples of such gases are air, oxygen, oxygen diluted with helium, argon, nitrogen, or other inert gas, oxygen-hydrocarbon mixtures and the like. It is preferred to employ gases containing 20 or more percent by weight molecular oxygen and even more preferred to employ gases containing 90 or more percent by weight molecular oxygen.

The activated carbon catalysts employed in the process of this invention are well known in the art and are available under a large number of trade names. These activated carbons are characterized by high adsorptive capacity for gases, vapors, various molecules dissolved in solution, and colloidal solids and relatively high specific surface areas. Carbon, char or charcoal is produced by destructive distillation of wood, peat, lignite, nut shells, bones, vegetable or other natural or synthetic carbonaceous matter, but must usually be "activated" to develop adsorptive power. Activation is usually achieved by heating to high temperatures (800°-900° C.) with steam or with carbon dioxide, which brings about a porous particle structure and increased specific surface area. In some cases hygroscopic acid or sodium sulfate, are added prior to the destructive distillation or activation, to increase adsorptive capacity. The carbon content of active carbons ranges from about 10% for bone charcoal to about 98% for some wood chars and nearly 100% for activated carbons derived from organic polymers. The non-carbonaceous matter in activated charcoal will vary depending on precursor origin and/or activation procedure. For example, inorganic "ash" components containing aluminum and silicon are oftentimes present in large amounts accompanied by certain alkali metals and alkaline earths. The later grouping influences the acidity-basicity characteristics of the activated carbon. Other inorganic constituents found in many activated carbons include iron and titanium. Depending on raw material original and activation procedure, large amounts of oxygen can be present along with lesser amounts of hydrogen, nitrogen and sulfur. Oxygen content also influences activated carbon acidity-basicity.

The specific surface area of activated carbons used herein, measured by the BET (Brunauer-Emmett-Teller) method using N₂ can range from 100 to nearly 2000 m²/g. The packed bulk density of activated carbons will depend on the form (powder vs. particulate) and also on the measuring technique employed. Measured values less than 0.15 g/cc and as high as about 0.6 g/cc for powders have been recorded.

The amount of granular or powdered activated carbon employed in the oxidation process can range from 0.5 to 100 or more parts by weight for every 100 parts by weight of the N-phosphonomethyliminodiacetic acid

employed. For the powdered activated carbons, it is preferred to employ from 1 to 50 parts by weight of activated carbon for 100 parts by weight of the N-phosphonomethyliminodiacetic acid. For the activated carbons in granular forms, it is preferred to employ 1 to 75 parts by weight per 100 parts by weight of N-phosphonomethyliminodiacetic acid and a more prescribed range is from 20 to 60 parts by weight. It is, of course, obvious that in a tubular type reactor, hereinbefore mentioned, weight ratios of activated carbon to reactants can vary over even greater ranges than herein set forth. The amount of zeolite encapsulated catalyst can be varied as found most effective, but will generally be in the range of 2 to 15 or 20 parts by weight (metal + zeolite) per 100 parts by weight carbon catalyst, and about 5 parts is a convenient amount. The activated carbon employed can be in the form of powders or granules, and the zeolite encapsulated catalyst can be in similar form. Further description of procedures for oxidizing N-phosphonomethyliminodiacetic acid are found in Hershman U.S. Pat. No. 3,969,398, the disclosure of which is incorporated herein by reference. The activated carbons disclosed by way of example in that patent can suitably be used for the present oxidations. The encapsulated zeolite catalyst can be mixed with the carbon catalyst prior to use as a co-catalyst in a process, or it can be added to a reaction medium to which a carbon catalyst is also added, and used as a co-catalyst therein. Of course, when both catalysts are in a reaction medium, they will become admixed therein, and generally will still be mixed together when recovered from the process, or used in recycle procedures.

The amount of zeolite encapsulated catalyst can also be considered with respect to the formaldehyde or other materials to be oxidized, and the medium containing materials to be oxidized, especially in the event waste streams are being treated subsequent to a reaction. While the catalyst can be used over broad ranges of concentrations, relatively low concentrations are often effective, such as in the range of about 0.01% to 0.5% or slightly higher, of the reaction medium, with the percentages being calculated on the total weight of platinum or other noble metal and zeolite present. The percentages, of course, would be much smaller if based on the small amount of catalytic metal present and encapsulated in the zeolite.

In illustrated reactions herein, the phosphonomethyl group has been shown with a free phosphonic acid, i.e., with two -OH groups on the phosphorus. However, the present catalyst system can be usefully employed in the presence of N-phosphonomethylamines in general, including those in which the phosphono moiety is in ester or in salt form; and similarly the diacetic acid groups in the iminodiacetic acid can be in ester or salt form, with operating reactants being illustrated



in which each R is individually selected from hydrogen, or salt or ester forming groups. Exemplifications of suitable ester forming groups are hydrocarbyl groups, particularly short-chain alkyl groups such as methyl and ethyl groups. Alkali metal, e.g., sodium or potassium, alkaline earth metal and ammonium salts can conveniently be used. The oxidation reaction is conveniently conducted in water, but other solvents can be employed, e.g., glacial acetic acid, aqueous acetic acid, or various other solvents which are resistant to oxida-

tion under the reaction conditions. Illustrative of other solvents or liquids which can be used are nitriles such as acetonitrile, propionitrile, etc.; nitrocompounds such as nitromethane, and halogenated compounds such as methylene chloride.

The microcrystalline supports used herein are three-dimensional aluminosilicates, zeolites, and it is advisable to select such materials so as to have sufficient acid stability as not to undergo excessive degradation (compositional and/or crystallinity changes) under the conditions of employment, such as in the presence of $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{NR}^1\text{R}^2$, where R^1 and R^2 are organic groups or hydrogen, in aqueous solution at elevated temperatures. Aluminosilicates with an Si/Al ratio of about 2 or more will generally have sufficient acid stability. Examples of zeolites which can be used include mordenite, zeolite Y, zeolite L, zeolite Ω , erionite, ferrierite, offretite, Silicalite, ZSM-5, etc. Additionally various two-dimensional layered materials can be used of the type $\text{Zr}(\text{O}_3\text{PR})_2$, where R includes $-\text{OH}$, $-\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, and $-\text{CH}_2\text{CH}_2\text{CH}_2\text{SO}_3\text{H}$.

Encapsulation methods for noble metal crystallites comprise a series of steps, in particular sequence, in order for the final catalyst to possess the distribution of crystallites residing entirely within the internal pore structure of the microcrystalline support. Three general methods are employed to incorporate the precursor complex within the support. The precursor complexes are selected from either various cationic metal amine species such as $\text{Pt}(\text{NH}_3)_4^{2+}$, $\text{Rh}(\text{NH}_3)_5\text{Cl}^{2+}$, $\text{Ir}(\text{NH}_3)_5\text{Cl}^{2+}$, $\text{Pd}(\text{NH}_3)_4^{2+}$, or $\text{Ru}(\text{NH}_3)_6^{3+}$ or suitable organometallic compounds including $\text{Pt}(\text{allyl})_2$, $\text{Pt}(1,5\text{-cyclooctadiene})_2$, $\text{Pt}(\text{ethylene})_3$, $\text{Rh}(\text{allyl})_3$, $\text{Ir}(\text{allyl})_3$, or $\text{Pd}(\text{allyl})_2$.

METHOD 1

A dilute ($<0.1\text{M}$) aqueous solution of the precursor compound exemplified by $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ is stirred with a slurry of the microcrystalline support (particle size typically less than 200 mesh) at room temperature or higher to effect an ion exchange between $\text{Pt}(\text{NH}_3)_4^{2+}$ and zeolite counterions such as NH_4^+ or Na^+ to the extent that $\text{Pt}(\text{NH}_3)_4^{2+}$ is incorporated within the support to ~ 0.1 to ~ 5.0 wt. % as Pt metal. Suitable supports for treatment by this ion-exchange method include the NH_4^+ or Na^+ forms of mordenite, zeolite Y, zeolite L, zeolite Ω (omega), and ZSM-5, although other monocations or mixtures of monocations in the zeolite may be used.

After an appropriate length of time, the $\text{Pt}(\text{NH}_3)_4^{2+}$ /zeolite material is filtered and washed with water until no chloride counterion is detected in the filtrate. The solid catalyst precursor material is then dried in a vacuum oven at $50^\circ\text{--}100^\circ\text{C}$. overnight then sieved to an appropriate particle size, typically below 200 mesh.

Preparation of the encapsulated catalyst from the $\text{Pt}(\text{NH}_3)_4^{2+}$ /zeolite precursor material is accomplished in a flow reactor with the solid located between quartz wool plugs. The solid precursor may be diluted with inert particles of low-surface area alumina or silica of typically 8–14 mesh to lower the pressure drop across the bed and improve gas-solid contacting. After the solid is equilibrated in the reactor under an inert argon gas purge at 100°C ., an atmosphere of O_2/Ar is provided with a total flow rate of the gas blend of 400 ml/min. with 80 ml/min. of O_2 and 320 ml/min. of Ar. The reactor furnace temperature is then increased at a

rate of between $0.2^\circ/\text{min.}$ and $10^\circ/\text{min.}$ up to at least 350°C . and as high as 600°C . in certain instances. The O_2 flow is then stopped after reaching the desired temperature and Ar-purged for at least 3 hr. while cooling the reactor to 300°C . Then a flow of H_2 at 80 ml/min. is introduced into the Ar stream and maintained for 2–3 hr. The reactor is then cooled to 100°C . under an Ar purge of less than 320 ml/min. The above procedure serves to decompose the Pt-amine complex and results in the encapsulation of small Pt crystallites within the internal zeolite pore structure.

The Pt dispersion and particle sizes are evaluated by means of transmission electron microscopy (TEM). Ultramicrotomed thin (100 Å) sections of the Pt/zeolite particles embedded in an epoxy matrix provide the best means of examination. Metal particle sizes must be less than the diameter of the largest void space within the zeolite microstructure in order to be considered "encapsulated". Typically, the metal particles are no greater than 20 Å in size.

METHOD 2

Alternatively, the zeolites described in Method 1 must be used in the NH_4^+ form and calcined in a flow reactor in O_2/Ar at 550°C . for 3 hr. or more. The anhydrous zeolite is then removed from the reactor and suspended in a predried hydrocarbon solvent such as hexane or toluene.

The metal is then introduced as a hydrocarbon-soluble complex [(e.g., $\text{Pt}(\text{allyl})_2$, $\text{Pt}(1,5\text{-cyclooctadiene})_2$, $\text{Pt}(\text{ethylene})_3$, $\text{Rh}(\text{allyl})_3$, $\text{Ir}(\text{allyl})_3$, or $\text{Pd}(\text{allyl})_2$] containing at least one ligand subject to elimination when contacted with the hydrocarbon slurry of the anhydrous zeolite. After stirring under a dry atmosphere for two or more days, the zeolite slurry is filtered then rinsed well with the hydrocarbon solvent. After drying at room temperature and under vacuum, the zeolite containing the adsorbed oxide-bound metal complex is treated under a H_2 or inert gas atmosphere in a flow reactor at $25^\circ\text{--}200^\circ\text{C}$. for a length of time necessary to decompose the complex. The catalyst so prepared may be evaluated via TEM as described in Method 1.

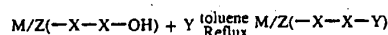
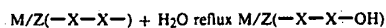
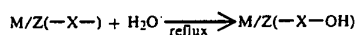
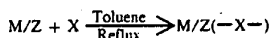
METHOD 3

For acid stable zeolites with pore openings consisting of ten or fewer Si and/or Al and oxygen atoms (ten member rings or less) or pore openings less than 6.5 Å it is generally necessary to entrap the metal precursor complex directly in the internal zeolite pore structure during the zeolite synthesis. Synthetic zeolites of this type include erionite, ferrierite, offretite, and ZSM-5 or its all-silica analogue, Silicalite. Zeolite syntheses are performed as prescribed in U.S. Pat. Nos. 2,950,952 (Zeolite T or erionite), 3,966,883 (ferrierite), 4,093,699 (offretite), 3,702,886 (ZSM-5), and 4,067,724 (silicalite), except that ~ 0.5 to ~ 2.0 wt. % as Pt of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$ (or other noble metal amine complex) is added to the synthesis mixture.

The $\text{Pt}(\text{NH}_3)_4^{2+}$ /zeolite catalyst precursor material obtained by this direct synthesis procedure is washed free of halide ions then optionally ion-exchanged at least three times with 2.2M NH_4Cl solution. After all halide ions are again rinsed free of the material, it is dried in a vacuum oven at $50^\circ\text{--}100^\circ\text{C}$. and sieved to an appropriate particle size, usually below 200 mesh. The encapsulated noble-metal zeolite composition is then obtained using the activation procedure described in Method 1.

For the encapsulated noble metal catalysts prepared using Method 1, it is desirable to perform the ion exchange of the metal complex cation on the NH_4^+ form of the zeolite in order for the final encapsulated catalyst to contain a high density of surface hydroxyl groups formed from decomposition of the NH_4^+ ions. The pore size and surface characteristics of those encapsulated metal/zeolite catalysts which may need further modification can be modified so as to discriminate between formaldehyde and various larger N-phosphonomethylamines such as $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{N}(\text{CH}_2\text{CO}_2\text{H})_2$ by the techniques outlined below.

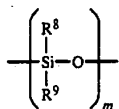
(1) Solution Modification. Various soluble reagents "X" are reacted with a hydrocarbon (e.g., toluene) slurry of the anhydrous metal/zeolite catalyst using some or all of the steps listed below. A list of suitable "X" reagents includes chlorosilane monomers of the form $\text{R}_x\text{SiCl}_{4-x-y-z}$ ($0 < x < 3$, $0 < y < 2$, $0 < z < 1$, R^3 methyl, ethyl, propyl, isopropyl, butyl, phenyl, and R^4 and R^5 may also be selected from the list for R^3 in various combinations) and chloro-terminated polydimethylsiloxane oligomers of the form $\text{ClSi}(\text{CH}_3)_2\text{O}-(\text{Si}(\text{CH}_3)_2\text{O})_n-\text{Si}(\text{CH}_3)_2\text{Cl}$ ($n=4, 5, 6$). The metal/zeolite catalyst is denoted as M/Z.



Steps (b) and (d) require vacuum dehydrations after their completion at $150^\circ\text{--}200^\circ\text{C}$. and less than 10^{-3} torr. Reagent Y is selected from various volatile trimethylsilyl-transfer agents such as $(\text{CH}_3)_3\text{SiCl}$ or $(\text{CH}_3)_3\text{SiNH-Si}(\text{CH}_3)_3$.

(2) Vapor-Phase Modification. The encapsulated metal/zeolite catalysts may also be modified by gas-phase reagents at temperatures above the boiling point of the reagent to 600°C . in a flow reactor. Reagents envisioned for use by this method include $(\text{CH}_3)_3\text{SiCl}$, $(\text{CH}_3)_3\text{SiNH-Si}(\text{CH}_3)_3$, $\text{Si}(\text{OR}^6)_4$ (R^6 =methyl, ethyl), and $\text{Ti}(\text{OR}^7)_4$ (R^7 =isopropyl, butyl).

(3) Catalyst Precursor Modification. Catalyst precursors prepared by means of Method 1 above may be impregnated after drying with various Si- or Ti-containing compounds including $\text{Si}(\text{OR}^6)_4$, $\text{Ti}(\text{OR}^7)_4$, and



where this silicone is of the type described in U.S. Pat. No. 4,402,867 and R^8 and R^9 are individually selected from the group consisting of hydrogen, methyl, fluorine, chlorine, and hydroxy, and m is an integer of at least 3. The impregnated catalyst precursor (e.g., $\text{Pt}(\text{NH}_3)_4^{2+}$ /zeolite) is then dried in a vacuum, sieved to the appropriate particle size, and charged to a flow

reactor. Treatment in O_2/Ar followed by H_2/Ar is identical to the procedure given in Method 1.

Oxidation procedures were conducted in a 300-ml 316 stainless steel "MagneDrive" autoclave from Autoclave Engineers. A continuous flow through the reactor of O_2 at 150–60 cc/min was used to purge the reactor of the CO_2 by-product. The extent of the oxidation was continuously monitored by the cumulative total of CO_2 in the O_2 off gas and detected using a Wilks Miran II Process Analyzer. Typically, a 2.0 ml charge of 37% formaldehyde solution was added to 98.0 ml of water and the mixture charged along with 0.10 to 0.25 g of catalyst. The N-phosphonomethylamine was added as a solid by means of injection with O_2 pressure into the reactor at the appropriate time without disassembling the autoclave. Formaldehyde could also be added in this fashion. Formaldehyde oxidations in the absence and the presence of the N-phosphonomethylamine were performed at $95 \pm 3^\circ\text{C}$, 30 psig O_2 (206.85 kPa at the flow rate given above, and 1500 rpm stirring rate).

EXAMPLE 1

A platinum-encapsulated catalyst was prepared by ion exchange of an aqueous slurry of Union Carbide LZM8, NH_4 -mordenite (NH_4 -MOR) in a 0.023M solution of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$. After stirring overnight the slurry was filtered then rinsed by resuspension in water followed by filtration until chloride ion was no longer detected in the filtrate. The $\text{Pt}(\text{NH}_3)_4^{2+}/\text{NH}_4$ -MOR catalyst precursor was vacuum dried overnight at 80°C . then sieved to below 200 mesh. A mixture of 1.5 g of $\text{Pt}(\text{NH}_3)_4^{2+}/\text{NH}_4$ -MOR and 7.0 cc of 8×14 mesh Al_2O_3 was charged to a quartz reactor tube and contained with quartz wool plugs. The reactor was equilibrated at 100°C . under ~ 10 cc/min Ar purge. With a flow of 80 cc/min O_2 and 320 cc/min. Ar, the reactor was increased in temperature at $0.2^\circ/\text{min}$. to 350°C . The O_2 flow was then discontinued as the reactor was cooled to 300°C . After 3 hr. a flow of 80 cc/min. H_2 was introduced into the 320 cc/min. gas stream for a 2 hr. period. The reactor was then cooled to 100°C . The 3.30% Pt/H-MOR catalyst so treated was recovered and found to have no Pt crystallites in excess of 20 \AA as seen from transmission electron microscopy.

The catalyst was evaluated in the 300-ml autoclave for formaldehyde oxidation as previously described and as summarized in Table 1. By comparison, a catalyst that is not encapsulated shows little formaldehyde oxidation activity once contacted with N-phosphonomethylglycine (see Table II). Additionally, as can be seen in the reaction data displayed between formaldehyde charges 10 and 14 in Table I these encapsulated catalysts differ from conventional supported noble metal catalysts (Pt/C) in that they can be washed free of adsorbed poisons (glyphosate) and this simple regenerative procedure restores the initial activity (charges 2 and 3 in Table I).

Mesh sizes given in Example 1 or elsewhere in the specification are those of the U.S. Standard Sieve Series.

TABLE I

Autoclave Evaluation Data for 3.30% Pt/H-MOR ^a for Formaldehyde Oxidation in the Absence and Presence of N-Phosphonomethylglycine		
Formaldehyde Charge No.	Reaction Time, Min.	Formaldehyde Conversion, %
1	51	87.3

TABLE I-continued

Autoclave Evaluation Data for 3.30% Pt/H—MOR ^a for Formaldehyde Oxidation in the Absence and Presence of N—Phosphonomethylglycine		
Formaldehyde Charge No.	Reaction Time, Min.	Formaldehyde Conversion, %
2 ^b	24	100.0
3 ^c	21	100.0
4	54	100.0
5	45	100.0
6	54	100.0
7 ^d	36	100.0
8	39	100.0
9 ^e	117	96.9
10	48	45.9
11 ^f	30	100.0
12	27	100.0
13	27	100.0
14 ^g	45	100.0
15	60	96.5
16	27	2.55
17 ^f	78	100.0
18	45	100.0
19	45	100.0
20 ^g	117	90.3
21	33	8.49

^aInitial autoclave charge: 0.10 g. Platinum loading determined by elemental analysis.^bTotal catalyst charge is now 0.25 g.^cAdded 0.20 g of N—phosphonomethylglycine.^dAdded another 0.20 g of N—phosphonomethylglycine; total charge: 0.40 g.^eResidual catalyst activity after stirring ~65 hr. in a solution of 0.40 g of N—phosphonomethylglycine.^fCatalyst filtered off, rinsed with water, and returned to the autoclave.

TABLE II

Autoclave Evaluation Data for ~2% Pt/CPG ^a for Formaldehyde Oxidation in the Absence and Presence of N—Phosphonomethylglycine		
Formaldehyde Charge Number	Reaction Time, Min.	Formaldehyde Conversion, %
1	21	100.0
2	21	100.0
3	21	100.0
4 ^b	37	9.3

^aCatalyst prepared with 100% controlled pore glass (CPG) of 200–400 mesh by incipient wetness method with aqueous Pt(NH₃)₂(NO₃)₂. Catalyst charge: 0.25 g.^bAdded 0.30 g of N—phosphonomethylglycine.

EXAMPLE 2

Some platinum-encapsulated catalysts require further functionalization in order to tailor the pore size and surface adsorption sites selectively to entry of formaldehyde into the internal pore structure in the presence of N-phosphonomethylglycine in the bulk solution. To illustrate this point a sample of Union Carbide NaY(L-ZY72) was thoroughly exchanged three times with 2.2M NH₄Cl solution. The NH₄Y zeolite was then exchanged with a 0.015M solution of Pt(NH₃)₄Cl₂. The Pt(NH₃)₄²⁺/NH₄Y precursor catalyst was dried in a vacuum oven at 80° C. overnight then sieved to below 200 mesh. The precursor catalyst was then charged to a quartz flow reactor between quartz wool plugs, purged with Ar at 100° C., and treated with O₂/Ar while the furnace temperature was ramped to 600° C. The thermal ramping rate was 2°/min. to 250° C. then 0.5°/min. up to 600° C. After 3-hr. purge in Ar while the reactor cooled to 300° C., an H₂/Ar gas mixture was passed through the catalyst bed for 2 hr. The reactor was cooled to 100° C. in an Ar gas purge.

The catalyst prepared by the above method showed significant poisoning within the time that two charges of formaldehyde were added in sequence. The results are shown in Table III.

TABLE III

Autoclave Evaluation Data for ~3% Pt/HY ^a for Formaldehyde Oxidation in Absence and Presence of N—Phosphonomethylglycine		
Formaldehyde Charge Number	Reaction Time, Min.	Formaldehyde Conversion, %
1	18	100.0
2	18	100.0
3	18	100.0
4 ^b	42	100.0
5	42	47.5

^aCatalyst charge: 0.10 g.^bAdded 0.20 g of N—phosphonomethylglycine.

In contrast, surface modification of the ~3% Pt/HY using chlorine-terminated polydimethylsiloxane (Cl—PDMSi—Cl, Petrarch Systems PS375) extended the number of formaldehyde oxidation cycles completed once N-phosphonomethylglycine was added. The Pt/HY catalyst was prepared using an identical procedure to the catalyst in Table III. However, after oxidation in O₂/Ar followed by reduction in H₂/Ar, the catalyst was recovered in an N₂-containing drybox. The catalyst powder was then treated with an excess of Cl—PDMSi—Cl, diluted with dry toluene, and refluxed overnight as a suspension in toluene. The treated catalyst designated ~3% Pt/HY(—PDMSi—) was filtered in air, washed with hexanes, and dried in a vacuum oven at 115° C. overnight. A sample of this catalyst gave the results shown in Table IV.

TABLE IV

Autoclave Evaluation Data for ~3% Pt/HY(—PDMSi—) ^a for Formaldehyde Oxidation in the Absence and Presence of N—Phosphonomethylglycine		
Formaldehyde Charge Number	Reaction Time, Min.	Formaldehyde Conversion, %
1	21	100.0
2 ^b	18	100.0
3	21	100.0
4	21	100.0
5 ^c	21	100.0
6	21	100.0
7 ^b	48	100.0
8	54	63.7

^aCatalyst charge: 0.15 g.^bAdded 0.20 g of N—phosphonomethylglycine.^cCatalyst filtered off, rinsed with water, and returned to autoclave.

The surface modified catalyst shown in Table IV extends the poisoning resistance by 2–3 cycles over the catalyst in Table III.

A co-catalyst as described herein can be usefully employed in processes to convert N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine under conditions in general effective for such conversion, including those taught in the referred-to U.S. Pat. No. 3,969,398. Thus the conversion can be carried out under conditions described in the following example.

EXAMPLE 3

To a 300 ml. autoclave as described above 100 ml. deionized water, 1 gram of Norit A activated carbon, and 4 grams N-phosphonomethyliminodiacetic acid are charged. There is also added a 0.15 gram amount of the 3.30% Pt/H—MOR catalyst of Example 1. The contents are heated to 90° C. with oxygen flowing at atmospheric pressure. The contents are heated to about 95° C. with agitation for approximately two hours, with yields of N-phosphonomethylglycine in excess of 95% expected to be obtainable. Because of the effectiveness of the noble metal catalyst in oxidizing the formaldehyde, the moles of CO₂ generated may be expected to

approach 1.9 or so for each mole of reactant, with the amount of formaldehyde remaining being less than 10% of theoretical and in concentrations possibly around 0.1% or lower by weight. Thus the tendency of formaldehyde to react with the N-phosphonomethylglycine product will be markedly diminished.

While the present encapsulated catalysts are of particular interest for oxidation of formaldehyde in the presence of N-phosphonomethylglycine or other products of oxidative cleavage reactions of N-phosphonomethylaminodiacetic acid or other glycine derivatives, the catalysts will also be useful for oxidation in the presence of other catalyst poisons having size and zeolite diffu-

sive oxidation of formaldehyde under practical conditions in the presence of such poison, in a reasonable time period, such as half-an-hour to an hour or so. Ethylenediaminetetracetic acid, quinaline and 4-methylquinoline are examples of nitrogen bases against which encapsulated catalysts can provide protection in accord with the present invention.

A number of catalysts were prepared in accord with procedures described herein, and their characterization by transmission electron microscopy is reported in Table V, along with that of a platinum on silica catalyst. The catalyst description includes the percentage of platinum in the catalyst.

TABLE V

Summary of Platinum Catalysts and Their Characterization by Transmission Electron Microscopy

Catalyst Description	Catalyst Support Particle Size ^a (μm)	TEM Data ^b	
		Pt Particle Sizes	Å Distribution ^c
1.79% Pt/SiO ₂	74-595 ^d	15-40	M
2.90% Pt/HY	1.47	10-20	M
3.23% Pt/HY(—PDMSi—) ^e	1.48	10-15	M
3.30% Pt/H—MOR	1.06	9-18	M
3.57% Pt/H—MOR	1.06	9-18	M
2.62% Pt/H—ZSM-5	5.90	10-15	M
3.54% Pt/H—ZSM-5	5.54	10-20	C
0.38% Pt/H—ZSM-5	5.54	13-40	C
3.1% Pt/H—ZSM-5	—	15-44	C
		75-200	

^aParticle size determined from Coulter Counter measurements and reported as the average value unless otherwise noted.

^bSpecimens were in most cases (100 keV) ultramicrotomed sections of the catalyst embedded in epoxy resin.

^cCodes for the observed metal dispersions: M = monomodal, C = continuous range of particle sizes.

^dParticle size range for microspheroidal silica, Grace Grade 56.

^ePDMSi = polydimethylsiloxane oligomer attached to the zeolite surface by the reaction between the reduced Pt/HY sample (surface silica hydroxyl groups) and chlorine-terminated PDMSi in dry toluene.

^fParticle size not determined.

sion characteristics like those of N-phosphonomethylglycine. Various amines and other nitrogen bases are capable of poisoning the noble metal oxidation catalysts, and encapsulation in porous carriers as taught herein is effective in avoiding or inhibiting such poisoning in a number of cases, particularly when the poison is a relatively large molecule, such as of molecular weight over 100, or even over 150. Even if poisoning is not avoided, the encapsulated catalyst may still show some improvement in activity and life over a catalyst in which the active metal has not been protected. The value of various degrees of improvement may depend upon the particular application. However, it is apparent that an encapsulated catalyst can be considered effectively protected against a particular poison in a formaldehyde oxidation, if it makes possible nearly quantita-

The effect of various nitrogen bases on formaldehyde oxidation with various platinum catalyst was determined and reported in Table VI below. All experiments were conducted in a 300-mL Autoclave Engineers Magnedrive autoclave run at 1500 rpm at a temperature of 95° C. and 30 psig O₂. A continuous flow of O₂ (mixed with CO₂ product) at 150-60 cm/min. afforded a means to monitor the conversion of the formaldehyde substrate with a calibrated Wilks Miran II Process Analyzer (IR detector). Typically 2.0 mL of 37% formaldehyde solution, 100-mL of water, and 0.10 to 0.50 g of catalyst was charged to the autoclave. Except where noted, 3.4 × 10⁻⁴ moles of nitrogen base were charged to the reactor. All Pt/zeolite samples used were in the "Pt-encapsulated" form. H₄EDTA = Ethylenediaminetetraacetic acid.

TABLE VI

Summary of the Effect of Various Nitrogen Bases on the Formaldehyde Oxidation Endpoint with Various Platinum Catalysts

Catalyst	No Base 100% Conversion (min.)	Endpoint (min.) with Nitrogen Base (% Conversion)				
		Glycine	H ₄ EDTA	Pyridine	Quinaline	4-methylquinoline
1.79% Pt/SiO ₂	45	60(5.2)	60(57.5)	39(6.7)	60(16.7)	—
2.93% Pt/HY	18	60(15.4)	60(52.8)	—	—	—
3.23% Pt/HY(—PDMSi—)	16	60(17.9)	15(100)	—	—	—
			18(100) ^a	—	—	—
			27(99.6)	—	—	—
			60(64.4)	—	—	—
3.5% Pt/H—MOR	20	60(55.5)	21(100)	60(89.2)	24(100)	—
			21(100)	60(74.2)	24(100)	—
			21(100)	—	24(100)	—
			—	—	21(100)	—
3.54% Pt/H—ZSM-5	20	60(75.1)	27(100)	60(20.3)	60(40.9)	18(100)

TABLE VI-continued

Summary of the Effect of Various Nitrogen Bases on the Formaldehyde Oxidation Endpoint with Various Platinum Catalysts						
Catalyst	No Base 100% Conversion (min.)	Endpoint (min.) with Nitrogen Base (% Conversion)				
		Glycine	H ₄ EDTA	Pyridine	Quinoline	4-methyl- quinoline
3.17% Pt/H—ZSM-5	18	60(78.8)	33(100) 36(99.5)	—	—	18(100)
		—	—	—	—	18(100)
		—	—	—	—	18(100)
		—	—	—	—	24(100)
		—	—	—	—	24(100)
		—	—	—	—	24(100) ^b
		—	—	—	—	27(100)
		—	—	—	—	27(100) ^c
		—	—	—	—	45(100)
		—	—	—	—	45(100)
		—	—	—	—	54(100) ^d
		—	—	—	—	54(100)

^aHere and in succeeding experiments, these data represent subsequent formaldehyde cycles with a fresh formaldehyde charge.

^b4-Methylquinoline total charge: 6.8×10^{-4} moles.

^c4-Methylquinoline total charge: 3.4×10^{-3} moles.

^dFormaldehyde oxidation endpoint after 24 hrs. in 0.034 M 4-methylquinoline.

I claim:

- The method of oxidizing formaldehyde or formic acid in the presence of an N-phosphonomethyl amine which comprises contacting a liquid solution containing formaldehyde or formic acid and an N-phosphonomethylamine with oxygen in the presence of a catalyst comprising a microporous support with a noble metal oxidation catalyst located within the pores of such support, with the support being a microporous acid resistant aluminosilicate having an Si to Al ratio of at least 2 and with the microporous support being selectively permeable so as to inhibit contact of the N-phosphonomethylamine with the noble metal therein, at a temperature sufficiently elevated to effect the desired oxidation.
- The method of claim 1 in which the formaldehyde or formic acid are produced as by-products in an oxidative cleavage reaction of an N-phosphonomethylamine to produce a different N-phosphonomethylamine compound, with such reaction involving use of an active carbon catalyst.
- The process of claim 1 in which the aluminosilicate is a zeolite of the mordenite class.
- The process of claim 1 in which the catalyst is a zeolite containing platinum crystallites within the pores and generally of diameters no greater than 20 Å as measured by transmission electron microscopy.
- The method of claim 1 in which the noble metal catalyst is used as a co-catalyst along with activated carbon catalyst to effect oxidative cleavage of N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine and concurrent oxidation of the formaldehyde by-product.
- The method of claim 5 in which the oxidation is conducted at temperatures of 25° to 200° C. and oxygen pressures of 50 to 20,000 kPa.
- The method of claim 5 in which the oxidation is conducted at temperatures of 75° to 150° C. and pressures of 100 to 700 kPa.
- The method of claim 1 in which the catalyst has been modified by a chlorosilane compound, a chloro-terminated siloxane oligomer, or a silicone polymer.
- The method of claim 1 in which the microporous support is a zeolite characterized by pore openings no greater than about 8 Å.
- The method of claim 1 in which the microporous support is characterized by pore openings no greater than about 5 Å and platinum has been incorporated in the zeolite during its preparation.
- The method of oxidizing formaldehyde of formic acid with a noble metal catalyst in a waste stream which comprises contacting a waste stream containing formaldehyde or formic acid with oxygen in the presence of a catalyst comprising a microporous support with a noble metal catalyst located within the pores of such support, with the support being a microporous, acid resistant aluminosilicate having an Si to Al ratio of at least 2, and with the waste stream also containing a poison for the noble metal and the microporous support being selectively permeable so as to inhibit contact of the poison with the metal therein.

* * * * *

[54] **PROCESS FOR PRODUCING
N-PHOSPHONOMETHYLGLYCINE SALTS**

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[73] Assignee: Monsanto Company, St. Louis, Mo.
[21] Appl. No.: 926,681
[22] Filed: Jul. 21, 1978

Related U.S. Application Data

- [63] Continuation-in-part of Ser. No. 753,232, Dec. 20, 1976, abandoned.
[51] Int. Cl.² C07F 9/38
[52] U.S. Cl. 260/501.12; 260/239 B;
260/326.11 R; 260/326.85; 260/502.5; 544/110;
544/78; 546/22
[58] Field of Search 260/239 B, 290 R, 293.87,
260/326.11 R, 326.85, 502.5, 501.12; 544/110,
78

[56]

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3,969,398 7/1976 Hershman 260/502.5
3,977,860 8/1976 Franz 260/239 B X

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[57]

ABSTRACT

Salts of N-phosphonomethylglycine are produced by forming a salt of N-phosphonomethyliminodiacetic acid with a salt-forming cation in an aqueous medium and then oxidizing the salt solution with an oxygen-containing gas in the presence of a platinum on activated carbon catalyst. The salts produced are useful as herbicides or plant growth regulants.

17 Claims, No Drawings

PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE SALTS

This application is a continuation-in-part of copending application Ser. No. 753,232, filed Dec. 20, 1976, now abandoned.

This invention relates to a method of producing certain mono and di salts of N-phosphonomethylglycine. More particularly, the invention is concerned with a method wherein such salts are produced by an oxidation reaction which provides high yields while minimizing or eliminating disadvantages of the prior art.

The preparation of such salts by reacting N-phosphonomethylglycine with the salt-forming cations of certain metals, ammonium or organic ammonium in aqueous solution is described in U.S. Pat. No. 3,977,860. Known procedures for preparing N-phosphonomethylglycine include oxidation of N-phosphonomethyliminodiacetic acid using such oxidizing agents as hydrogen peroxide, nitric acid, peroxyacetic acid and oxidation in aqueous media, e.g., water solutions using a free oxygen-containing gas and a noble metal catalyst such as platinum, palladium, rhodium, etc. as described in U.S. Pat. No. 3,950,402 or an activated carbon catalyst as described in U.S. Pat. No. 3,969,398. According to these patents, it is preferred to employ approximately saturated solutions of the N-phosphonomethyliminodiacetic acid in water at the temperature of reaction for ease of reaction and ease of recovery of the product. The saturated aqueous solution contains at most about 1 percent by weight of the acid at 25° C., about 4 percent by weight at 95° C. and about 10 percent by weight at 150° C. Such relatively low solubility of the acid in water severely restricts the amount of N-phosphonomethyliminodiacetic acid which can be charged and oxidized in a batch reaction system to form the desired N-phosphonomethylglycine. In order to recover the N-phosphonomethylglycine from the aqueous solution, water has to be distilled off and this requires the expenditure of considerable heat energy.

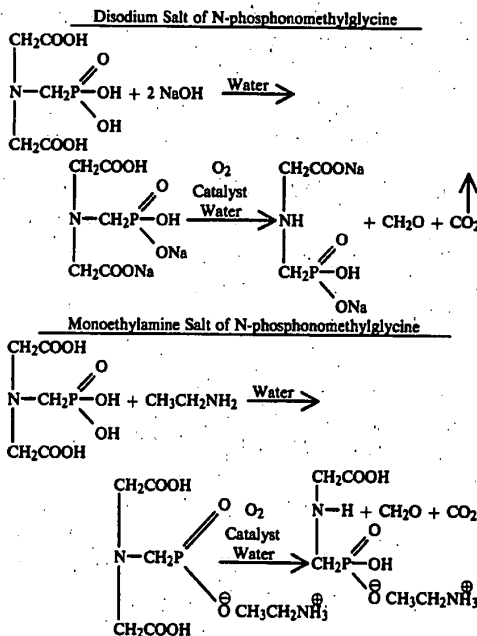
It has now been found that the salts of N-phosphonomethylglycine can be readily prepared using a single aqueous reaction system in which a salt of N-phosphonomethyliminodiacetic acid is oxidized by a molecular oxygen-containing gas in the presence of a noble metal oxidation catalyst. The mono and di salts of N-phosphonomethylglycine which are produced by this method are those wherein the salt-forming cation is selected from the group consisting of the cations of alkali metals, alkaline earth metals, ammonium and organic ammonium provided that when the organic group is aryl, the ammonium salt is a primary amine salt.

The term "alkali-metal" encompasses lithium, sodium, potassium, cesium and rubidium, and the term "alkaline earth metal" includes beryllium, magnesium, calcium, strontium and barium.

The organic ammonium salts of the above type are those prepared from low molecular weight organic amines, i.e., having a molecular weight below about 300, and such organic amines include: the alkyl amines, alkylene amines and alkanol amines containing not more than 2 amine groups, such as methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, isobutylamine, sec-butylamine, n-amylamine, isoamylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexa-

decylamine, heptadecylamine, ctadecylamine, methylethylamine, methylisopropylamine, methylhexylamine, methylnonylamine, methylpentadecylamine, methyloctadecylamine, ethylbutylamine, ethylheptylamine, ethyloctylamine, hexylheptylamine, hexyloctylamine, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-amylamine, diisoamylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-secbutylamine, tri-n-amylamine, ethanolamine, n-propanolamine, isopropanolamine, diethanolamine, N,N-diethylethanolamine, N-ethylpropanolamine, N-butylethanolamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl-2-amine, di-butenyl-2-amine, n-hexenyl-2-amine and propylenediamine; primary aryl amines such as aniline, methoxyaniline, ethoxyaniline, o,m,p-toluidine, phenylenediamine, 2,4,6-tribromoaniline, benzidine, naphthylamine, o,m,p-chloroaniline, and the like; and heterocyclic amines such as pyridine, morpholine, piperidine, pyrrolidine, indoline, azepine and the like.

In the aforescribed aqueous reaction system, the charged reactants initially form the mono or di salts of N-phosphonomethyliminodiacetic acid (depending on the stoichiometry), and these salts as formed are then oxidized to N-phosphonomethylglycine salts as indicated below for the disodium salt and the monoethylamine salt, respectively.



By the term "molecular oxygen-containing gas", as employed herein, is meant any gas containing molecular oxygen with or without diluents which are non-reactive with the oxygen or with the reactant or product under the conditions of reaction. Examples of such gases are air, oxygen, oxygen diluted with helium, argon, nitrogen, or other inert gas, oxygen-hydrocarbon mixtures and the like. It is preferred to employ gases containing 20 or more percent by weight molecular oxygen and even more preferred to employ gases containing 90 or

more percent by weight molecular oxygen. It is, of course, obvious to those of ordinary skill in the art that when molecular oxygen-containing gases containing other inert gases are employed, the pressures should be increased to insure adequate partial pressures of oxygen in the system to maintain a sufficient rate of reaction.

The amount of the molecular oxygen-containing gas employed can vary over wide ranges. It is, of course, obvious to those skilled in the art that the best yields of the N-phosphonomethylglycine salts are produced when at least stoichiometric amounts of oxygen are employed. In most instances for ease of reaction and best yield of the final product, the amount of oxygen employed would ordinarily be at least $\frac{1}{2}$ mole of oxygen for each mole of N-phosphonomethyliminodiacetic acid salt. In actual practice, the amount of oxygen employed will be from $\frac{1}{2}$ to 1 or more moles for each mole of the N-phosphonomethyliminodiacetic acid salt since the efficiency of the oxygen utilization is usually less than 100 percent.

The noble metal oxidation catalyst used in the method of this invention is platinum, and such metal is supported on an activated carbon substrate. The activated carbon supports which can be employed are commercially available under a wide variety of trade names, and the manner in which the metal is placed on the substrate is well understood in the art. Many of the useful activated carbon supports are described in detail in U.S. Pat. No. 3,969,398.

In conducting the process of this invention, it is preferred to employ approximately saturated solutions of the N-phosphonomethyliminodiacetic acid salt in water at the temperature of reaction for ease of reaction and ease of recovery of the product, N-phosphonomethylglycine salt. The temperature employed in carrying out the process of this invention should be sufficient to initiate the reaction and to sustain the reaction once initiated. Temperatures of from about 25° C. to 150° C. or even higher are usually satisfactory. As those skilled in the art would realize, at lower temperatures the rate of reaction may be undesirably slow and, therefore, temperatures of at least 75° C. are preferred and even more preferred are temperatures in the range of about 90° C. to 150° C.

The oxidation reaction is conducted at superatmospheric pressures, and it is preferred that a range of about 1.5 to 5 Kg/cm² be employed. Such pressures enable the reaction to proceed to substantial completion in a relatively few hours. Use of pressures greater than 5 Kg/cm² is feasible providing the reaction vessel is properly selected.

As noted above, the related oxidation processes of the prior art employ N-phosphonomethyliminodiacetic acid as the starting material, and the very low aqueous solubility of this acid severely restricts the quantity of product which can be obtained from any given volume of water. In addition, removal of the large amounts of water by distillation in order to isolate said product requires a correspondingly large expenditure of energy.

Another problem in the prior art processes is the presence of formaldehyde which is a co-product in the oxidation reaction. This co-product must also be removed by distillation, and it is then subjected to aerobic

oxidation before disposal in order to comply with environmental regulations. The presence of the formaldehyde co-product during the oxidation reaction is also undesirable since it contributes to and accelerates the formation of by-products such as N-methyl-N-phosphonomethylglycine and methylaminomethylphosphonic acid which are difficult to separate from the desired product. Although azeotropic distillation of the formaldehyde from the reaction mixture could be employed during the reaction itself, this would require added equipment and would not resolve the matter of subsequent disposal.

In accordance with the present invention, it has been found that the disadvantageous features of the prior art can be minimized or eliminated by the oxidation of a salt of N-phosphonomethyliminodiacetic acid using a platinum on activated carbon catalyst to yield a salt of N-phosphonomethylglycine.

The test procedures hereinafter described were employed to demonstrate the performance of the process of this invention. It should be understood that the specific details of each test are illustrative only and should not be construed as a limitation upon the scope of the invention. For comparison purposes, these test procedures were also carried out with various catalysts of the prior art.

For each of the runs tabulated below, the reaction vessel was a thick walled, 500 ml. glass bottle mounted on a Parr shaker. The bottle included an outer explosion shield which was wrapped with electrical heating tape, and the heating was controlled by a Variac transformer. A metal dial thermometer was inserted through a hole in the explosion shield and measured "outside" temperatures in terms of a relatively narrow range. The temperatures inside the reaction vessel itself were considered to be about 10° C. below said "outside" temperatures when the latter were measured in the 90°-110° C. range.

In each run, measured amounts of the N-phosphonomethyliminodiacetic acid and the base or cation contributor were added to 100 ml. of hot water in the bottle, the catalyst was added, and the reaction mixture was heated to a selected temperature. The bottle was pressurized with oxygen to a gauge pressure of 2.11 Kg/cm², bled down to atmospheric pressure, repressurized to the desired pressure and agitated on the shaker during the reaction period. Reaction pressure was carefully monitored, and after each increase of 0.35 Kg/cm² over the desired pressure, the reactor was bled to zero gauge pressure and then repressurized to the original starting level. This prevented an excessive accumulation of the CO₂ formed during the oxidation.

The course of the reaction was followed by periodic centrifugation of a small volume of the reaction mixture, acidification of the resultant clear solution with an equal volume of concentrated HCl, and determination of the proton NMR spectrum. In the tabulation of test results, the "% Unreacted Salt" in the product is based on said NMR analysis and indicates the degree of completion of the reaction in the specified time. Where "% Yield" is given, this indicates the amount of N-phosphonomethylglycine salt determined by U.V. analysis. All parts and percentages below are by weight unless otherwise stated.

Run	Starting Materials (gm./100 ml H ₂ O)			Reaction Conditions			Reaction Product		
	Acid	Base	Catalyst	hrs.	Kg/cm ²	°C.	% Unreacted Salt	% Yield	Comments
A	12.0	IPA 3.15	5% Pt/C 0.5	3.0	2.11	102-109	9	—	Formaldehyde = 30% theory By-product I = 2-3%
B	12.0	IPA 3.15	5% Pt/C 1.0	1.5	2.11	102-110	0	—	Formaldehyde = 32% theory By-product I = trace Very clean NMR
C	18.0	IPA 4.8	5% Pt/C 1.5	2.25	2.11	109-111	1	—	Formaldehyde = 20% theory By-product I = small amount Clean NMR
D	24.0	IPA 6.3	5% Pt/C 2.0	2.5	2.11-2.81	108-114	6	—	Formaldehyde = 14% theory By-product I = 3%
E	12.0	IPA 3.15	5% Pt/C 1.0	1.75	2.11	106-110	0	98	Formaldehyde = 30% theory By-product I = trace Very clean NMR
F	18.0	IPA 4.5	5% Pt/C 2.0	2.2	2.11	105-111	0	94	Formaldehyde = 16% theory By-product I = trace Very clean NMR
G	22.5	IPA 5.7	5% Pt/C 3.0	2.2	2.11	105-112	0	92	Formaldehyde = 12% theory By-product I = trace Very clean NMR
H	27.0	IPA 6.8	5% Pt/C 3.0	2.5	2.11	105-111	0	89	Formaldehyde = 10% theory By-product I = small amount By-product II = small amount Clean NMR
I	4.5	IPA 1.15	5% Pt/C 0.5	1.25	2.11	104-110	0	95	Formaldehyde = 25% theory No obvious by-products Very clean NMR
J	12.0	TMA 11.5	5% Pt/C 1.0	1.25	2.11	104-112	0	95	Formaldehyde = 1% theory Very clean NMR
K	13.5	30% NH ₃ 1.0	5% Pt/C 1.5	1.5	2.11	104-106	0	92	Formaldehyde = 20% theory Very clean NMR
L	12.0	25% DMA 9.0	5% Pt/C 1.0	1.25	2.11	104-110	0	93	Formaldehyde = 25% theory Clean NMR
M	12.0	86% KOH 3.0	5% Pt/C 1.0	1.5	2.11	104-115	0	94	Formaldehyde = 1% theory By-product II = small amount Very clean NMR
N	13.5	86% KOH 3.7	5% Pt/C 1.5	1.0	2.11	104-112	0	96.5	Formaldehyde = 3-4% theory Very clean NMR
O	4.5	86% KOH 1.3	5% Pt/C 1.0	17.0	2.11	24-26	0	—	No formaldehyde Clean NMR
P	1.15	86% KOH 0.55	5% Pt/C 0.25	3.0	2.11	25	45	—	Formaldehyde = 15-20% theory Clean NMR
Q	12.0	IPA 3.15	5% Rh/C 0.5	2.0	2.11	104-109	11	—	Formaldehyde = 70% theory By-product I = 5-8%
R	13.5	IPA 3.35	5% Rh/C 1.5	1.75	2.11	104-112	0	88	Formaldehyde = 25% theory By-product I = 2-3% Light yellow filtrate
S	13.5	IPA 3.35	5% Rh/C 1.5	1.0	2.11	109-110	0	—	Formaldehyde = 34% theory By-product I = 3-4% By-product II = small amount Yellow filtrate
T	12.0	IPA 3.15	5% Pd/C 0.5	3.0	2.11	102-109	5	—	Formaldehyde = 36% theory By-product I = 10% Yellow filtrate
U	13.5	IPA 3.35	5% Pd/C 1.5	1.0	2.11	104-106	0	84	Formaldehyde = 82% theory By-product I = 2.5% By-product II = trace Yellow filtrate
V	4.5	IPA 1.15	5% Pt/Al ₂ O ₃ 0.5	2.5	2.11	103-109	43	—	Formaldehyde = 5% theory Clean NMR
W	6.0	IPA 1.6	F-1A 0.5	2.0	2.11	90-95	0	97	Formaldehyde = 100% theory By-product I = trace Very clean NMR
X	12.0	IPA 3.15	F-1A 0.6	2.0	2.11	102-109	8	—	By-product I = 5-8%
Y	12.0	IPA 3.15	NORIT 1.0	2.0	2.11	106-108	0	67	By-product I = significant amount By-product II = significant amount
Z	4.5	IPA 1.15	NORIT 1.15	1.25	2.11	104-110	0	93	Formaldehyde = 100% theory By-product II = trace
AA	12.0	IPA 3.05	F-1C 1.0	2.0	2.11	104-112	0	65	By-product I = extensive By-product II = extensive Yellow filtrate
BB	13.2	IPA 3.35	NORIT 1.5	1.07	2.11	104-109	2	78	By-product I = significant amount By-product II = significant amount

-continued

Run	Starting Materials (gm./100 ml H ₂ O)			Reaction Conditions			Reaction Product		
	Acid	Base	Catalyst	hrs.	Kg/cm ²	°C.	% Unreacted Salt	% Yield	Comments
CC	13.5	IPA 3.35	F-6 1.5	3.0	2.11	104-110	46	—	Slightly yellow filtrate Formaldehyde = 22% theory
DD	13.5	IPA 3.35	F-7 1.5	3.0	2.11	104-110	29	—	By-product I = 3.5% Formaldehyde = 70% theory By-product I = 9% Light yellow filtrate
EE	13.5	IPA 3.35	F-8 1.5	2.0	2.11	104-112	20	—	Formaldehyde = 70% theory By-product I = 6% Light yellow filtrate
FF	13.5	IPA 3.35	F-9 1.5	2.0	2.11	104-112	15	—	Formaldehyde = 90% theory By-product I = 5% Slight yellow filtrate
GG	13.5	IPA 3.35	F-10 1.5	1.0	2.11	104-112	0	79	Formaldehyde = 85% theory By-product I = 6% Slightly yellow filtrate
HH	13.5	86% KOH 3.7	NORIT 1.5	1.0	2.11	104-109	0	79	Clear NMR Formaldehyde = 75% theory By-product I = 6% By-product II = trace

In Run P, the starting materials were added to 25 ml. of hot water in a 100 ml. glass bottle. As regards the base employed, IPA designates isopropylamine, TMA designates trimethylamine and DMA designates dimethylamine. By-product I is N-methyl-N-phosphonomethylglycine, and by-product II is methylaminomethylphosphonic acid. The noble metal catalysts employed are all commercial products, and the same is true of the activated carbon catalyst Norit A. The various F designated catalysts are all activated carbons prepared as described below.

F-1A

Norit A (10 gm.), distilled water (100 ml.) and conc. HCl (100 ml.) were refluxed for 40 hours, cooled to room temperature and filtered. The residue was washed with distilled water and then with very diluted ammonia until the filtrate was neutral. The product was washed once more with a large volume of water and then dried at 100° C. for 1.5 days.

F-1C

Norit A (100 gm.), distilled water (200 ml.) and conc. HCl (100 ml.) were refluxed with stirring for 40 hours, cooled to room temperature and filtered. The product was washed and dried as described for F-1A. This product (21 gm.), distilled water (100 ml.) and conc. HCl (100 ml.) were refluxed with agitation for 40 hours, filtered hot and the residue washed with a large volume of boiling distilled water until the filtrates were neutral. The product was dried to constant weight at 115° C.

F-6

A ground mixture of sucrose (50 gm.) and urea (5 gm.) was gradually pyrolyzed in a porcelain crucible and the residue annealed at a red heat for 50 minutes. The grey-black product resembled graphite more than charcoal.

F-7

A mixture of annealed lampblack (7.5 gm.), sublimed ferric chloride (1.5 gm.), urea (5 gm.) and water (25 ml.) was concentrated at reduced pressure and the residue ground to a powder. The latter was annealed in a porcelain crucible at a red heat for 30 minutes. The cooled product was washed repeatedly with a mixture of 250

ml. of boiling water and 25-50 ml. of conc. HCl until the filtrates were colorless. The material was then washed with boiling water until the filtrates were neutral. The product was dried at 110° C. for 3 days.

F-8

A ground mixture of sucrose (50 gm.), urea (5 gm.) and sublimed ferric chloride (1.5 gm.) was gradually pyrolyzed and the residue annealed at a red heat for 30 minutes. The product was ground to a powder and extracted with hot dilute HCl until the filtrates were colorless. The residue was then washed with boiling water until the filtrates were neutral and finally dried to constant weight at 110° C.

F-9

F-8 carbon catalyst (3 gm.) was extracted with conc. HCl until the filtrates were colorless. The initial filtrates are yellow due to ferric chloride formed from iron which is not extracted with hot dilute HCl. The material was then washed with a large volume of boiling water until neutral and dried to constant weight at 110° C.

F-10

Norit A (3 gm.) was extracted with conc. HCl, washed and dried as described for F-9 catalyst.

The data presented in the table demonstrates the several advantages of the present invention. Using the low payloads which the prior art processes suggest, a comparison of Run I with Runs W and Z show the yields with the instant platinum on carbon catalyst are about the same as those with the activated carbons alone. However, said platinum on carbon catalyst provides concurrent oxidation of the formaldehyde co-product as it is formed. Thus the time and expense required to remove said co-product from the final reaction product is significantly reduced.

When the payloads are increased by a factor of two or three, Runs E, J, L and N show that the platinum on carbon catalyst continues to give a yield of desired product at a 90% or greater level. However, a similar increase in payload with an activated carbon catalyst gives yields below 80% as shown in Runs Y, AA and

HH. Further, since the activated carbon catalysts alone do not provide for concurrent oxidation of the formaldehyde, the presence of the latter causes increased production of the undesirable by-products. Runs F, G and H show that still higher payloads can be employed with the platinum on carbon catalyst without any adverse effect on the % yield obtained. In addition, these higher payload runs also show relatively low levels of formaldehyde co-product with minimal by-product formation.

Returning to the increased payload Runs E, J, L and N with the platinum on carbon catalyst of this invention, it can be seen that they also compare favorably with corresponding Runs R and U which employed rhodium and palladium, respectively, on carbon. The other noble metal runs are characterized by somewhat reduced yields, along with some increase in co-product and by-product formation. The use of rhodium or palladium also gives rise to a discolored yellow filtrate in the product whereas the runs with the platinum on carbon catalyst regularly gives a colorless filtrate.

While the invention has been described herein with regard to certain representative examples for the purpose of illustrating its practice, those skilled in the art will readily recognize the variations and modifications which can be made without departing from the spirit and scope thereof.

What is claimed is:

1. Process for preparing a mono or di salt of N-phosphonomethylglycine wherein the salt-forming cation is selected from the group consisting of cations of alkali metals, alkaline earth metals, ammonium and organic ammonium, provided that when the organic group is aryl, the ammonium salt is a primary amine salt, which comprises contacting, at superatmospheric pressure, an aqueous solution of a corresponding mono or di salt of N-phosphonomethyliminodiacetic acid with an oxygen-containing gas in the presence of an oxidation catalyst which is platinum on activated carbon.

2. Process as defined in claim 1 wherein said superatmospheric pressure is at least about 1.5 Kg/cm².

3. Process as defined in claim 1 wherein said contacting is carried out at a temperature of from about 25° C. to 150° C.

4. Process as defined in claim 3 wherein said contacting is carried out at a temperature of at least about 90° C.

5. Process as defined in claim 1 wherein said salt-forming cation is alkali metal.

6. Process as defined in claim 1 wherein said salt-forming cation is said organic ammonium.

7. Process as defined in claim 1 wherein said contacting is carried out with the monoisopropylamine salt of N-phosphonomethyliminodiacetic acid.

8. Process as defined in claim 1 wherein said contacting is carried out with the mono(dimethylamine)salt of N-phosphonomethyliminodiacetic acid.

9. Process as defined in claim 1 wherein said contacting is carried out with the monopotassium salt of N-phosphonomethyliminodiacetic acid.

10. Process as defined in claim 1 wherein said contacting is carried out with the mono(trimethylamine)salt of N-phosphonomethyliminodiacetic acid.

11. Process as defined in claim 1 wherein said contacting is carried out with the monoammonium salt of N-phosphonomethyliminodiacetic acid.

12. Process as defined in claim 1 wherein said superatmospheric pressure is at least about 1.5 Kg/cm², and said contacting is carried out at a temperature of from about 90° C. to 150° C.

13. Process as defined in claim 12 wherein said contacting is carried out with the monoisopropylamine salt of N-phosphonomethyliminodiacetic acid.

14. Process as defined in claim 12 wherein said contacting is carried out with the mono(dimethylamine)salt of N-phosphonomethyliminodiacetic acid.

15. Process as defined in claim 12 wherein said contacting is carried out with the monopotassium salt of N-phosphonomethyliminodiacetic acid.

16. Process as defined in claim 12 wherein said contacting is carried out with the mono(trimethylamine)salt of N-phosphonomethyliminodiacetic acid.

17. Process as defined in claim 12 wherein said contacting is carried out with the monoammonium salt of N-phosphonomethyliminodiacetic acid.

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United States Patent [19]

Riley et al.

[11] Patent Number: 4,965,402

[45] Date of Patent: Oct. 23, 1990

[54] **PROCESS FOR PRODUCING
N-PHOSPHONOMETHYLGLYCINE**

[75] Inventors: Dennis P. Riley, Chesterfield; Willie J. Rivers, Jr., University City, both of Mo.

[73] Assignee: Monsanto Company, St. Louis, Mo.

[21] Appl. No.: 311,786

[22] Filed: Feb. 17, 1989

Related U.S. Application Data

[62] Division of Ser. No. 112,594, Oct. 26, 1987, Pat. No. 4,853,159.

[51] Int. Cl.⁵ C07F 9/38

[52] U.S. Cl. 562/17

[58] Field of Search 562/17

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Primary Examiner—J. E. Evans
Attorney, Agent, or Firm—Linda L. Lewis; Frank D. Shearin

[57] **ABSTRACT**

A process for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid using a molecular oxygen-containing gas in the presence of a transition metal catalyst.

7 Claims, No Drawings

PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE

This application is a division of application 5
07/112,594 filed Oct. 26, 1987, now U.S. Pat. No.
4,853,159 issued Aug. 1, 1989.

FIELD OF THE INVENTION

This invention relates to a process for producing 10
N-phosphonomethylglycine by the oxidation of N-
phosphonomethyliminodiacetic acid using transition
metal catalysts. More particularly, this invention relates
to a reaction using molecular oxygen and a transition
metal salt catalyst.

SUMMARY OF RELATED ART

It is known in the art that N-phosphonomethylgly-
cine can be produced by oxidizing N-phosphonome-
thyliminodiacetic acid using various oxidizing methods. 20
U.S. Pat. No. 3,950,402 discloses a method wherein
N-phosphonomethyliminodiacetic acid is oxidized to
N-phosphonomethylglycine in aqueous media using a
free oxygen-containing gas and a heterogeneous noble
metal-based catalyst such as palladium, platinum or
rhodium. U.S. Pat. No. 3,954,848 discloses the oxidation
of N-phosphonomethyliminodiacetic acid with hydro-
gen peroxide and an acid such as sulfuric or acetic acid.
U.S. Pat. No. 3,969,398 discloses the oxidation of N-
phosphonomethyliminodiacetic acid using molecular
oxygen and a heterogeneous activated carbon catalyst.
Hungarian Patent Application No. 011706 discloses the
oxidation of N-phosphonomethyliminodiacetic acid
with peroxide in the presence of metals or metal com-
pounds.

R. J. Motekaitis, A. E. Martell, D. Hayes and W. W.
Frenier, Can. J. Chem., 58, 1999 (1980) disclose the
iron(III) or copper(II) catalyzed oxidative dealkylation
of ethylene diaminetetracetic acid (EDTA) and nitrilo-
triacetic acid (NTA), both of which have iminodiacetic
acid groups. R. J. Motekaitis, X. B. Cox, III, P. Taylor,
A. E. Martell, B. Miles and T. J. Tvedt, Can. J. Chem.,
60, 1207 (1982) disclose that certain metal ions, such as
Ca(II), Mg(II), Fe(II), Zn(II) and Ni(II) chelate with
EDTA and stabilize against oxidation, thereby reducing 45
the rate of oxidative dealkylation.

SUMMARY OF THE INVENTION

The present invention involves a process for the pro-
duction of N-phosphonomethylglycine comprising con- 50
tacting N-phosphonomethyliminodiacetic acid with a
molecular oxygen-containing gas in the presence of a
transition metal catalyst.

DETAILED DESCRIPTION OF THE INVENTION

The process of this invention involves contacting
N-phosphonomethyliminodiacetic acid with a transition
metal catalyst in a mixture or solution. This mixture or
solution is contacted with a molecular oxygen-contain- 60
ing gas while heating the reaction mass to a temperature
sufficiently elevated to initiate and sustain the oxidation
reaction of N-phosphonomethyliminodiacetic acid to
produce N-phosphonomethylglycine.

The transition metal catalyst of the present invention 65
can be any one or more of several transition metal com-
pounds such as manganese, cobalt, iron, nickel, chro-
mium, ruthenium, aluminum, molybdenum, vanadium

and cerium. The catalysts can be in the form of salts
such as manganese salts, e.g., manganese acetate, man-
ganese sulfate; complexes such as manganese(II)bis(ace-
tylacetonate) (Mn(II)(acac)_2); cobalt salts such as Co-
(II)(SO_4), Co(II)(acetylacetonate), CoCl_2 , CoBr_2 , Co-
(NO_3)₂ and cobalt acetate; cerium salts such as
(NH_4)₄Ce(SO_4) and (NH_4)₂Ce(NO_3)₆; iron salts such as
(NH_4)₂Fe(SO_4)₂, iron(III)(dicyano)-(bisphenan-
throline)₂-(tetrafluoro)borate salt and $\text{K}_3\text{Fe(CN)}_6$ and
other metal salts such as NiBr_2 , CrCl_3 , $\text{RuCl}_2(\text{Me}_2\text{SO})$,
 RuBr_3 , $\text{Al(NO}_3)_3$, $\text{K}_4\text{Mo(CN)}_8$, $\text{VO(acetylacetonate)}_2$
and VOSO_4 . The catalyst can be added to the N-phos-
phonomethyliminodiacetic acid in the salt form, or a
salt may be generated in situ by the addition of a
source of a transition metal ion such as MnO_2 which
dissolves in the reaction medium. The Mn(III)-
chloro(phthalocyaninato), however, is not catalytic,
possibly because the phthalocyanine ligand covalently
bonds to the Mn(III) and therefore inhibits the forma-
tion of N-phosphonomethyliminodiacetic acid/ manga-
nese complex in solution.

Manganese salts such as Mn(II), Mn(III) or Mn(IV)
salts can be used individually, however, the reaction
displays a delayed reaction initiation time (initiation
period), e.g., there is a delay, before any N-phos-
phonomethylglycine is produced. When a mixture of
Mn(II) and Mn(III) salts are used as a catalyst system,
the initiation is diminished or eliminated. A preferred
manganese salt catalyst is a mixture of Mn(II) and
Mn(III) salts in the range of 1:10 to 10:1 mole ratio of
the Mn ions. A most preferred manganese catalyst salt is
a 1:1 mole ratio of Mn(II) and Mn(III) ions in the form
of manganese acetate salts. A preferred cobalt catalyst
is a Co(II) salt such as Co(II)(SO_4), Co(II) Cl_2 , Co-
(II) Br_2 , Co(II)(OH)₂ and Co(II)acetate.

The concentration of the transition metal catalyst in
the reaction solution can vary widely, in the range of
0.1M to 0.0001M total metal ion concentration. For
manganese, the reaction appears to have a first order
dependency on the catalyst concentration, e.g., the
reaction rate increases linearly as the catalyst concen- 40
tration increases. The preferred concentration is in the
range of about 0.01M to about 0.001M, which gives a
suitably fast rate of reaction that can be easily con-
trolled and favors selectivity to N-phosphonomethylgly-
cine.

The reaction temperature is sufficient to initiate and
sustain the oxidation reaction, in the range of about 25°
C to 150° C. In general, as the reaction temperature
increases, the reaction rate increases. To achieve an
easily controlled reaction rate and favor selectivity to
N-phosphonomethylglycine, a preferred temperature
range is about 50° C. to 120° C. and a most preferred is
in the range of about 70° C. to 100° C. If a temperature
of above about 100° C. is used, pressure will have to be
maintained on the system to maintain a liquid phase.

The pressure at which this process is conducted can
vary over a wide range. The range can vary from about
atmospheric (101 kPa) to about 3000 psig (20700 kPa).
A preferred range is about 30 psig (200 kPa) to about
1000 psig (about 6900 kPa). A most preferred range is
from about 150 psig (about 1000 kPa) to 600 psig (about
4140 kPa).

The oxygen concentration, as designated by the par-
tial pressure of oxygen (PO_2), in the reaction affects the
reaction rate and the selectivity to the desired product,
N-phosphonomethylglycine. As the PO_2 increases, the
reaction rate generally increases and the selectivity to

N-phosphonomethylglycine increases. The PO₂ can be increased by increasing the overall reaction pressure, or by increasing the molecular oxygen concentration in the molecular oxygen-containing gas. The PO₂ can vary widely, in the range of from 1 psig (6.9 kPa) to 3000 psig (20700 kPa). A preferred range is from 30 psig (207 kPa) to 1000 psig (6900 kPa).

The term "molecular oxygen-containing gas" means molecular oxygen gas or any gaseous mixture containing molecular oxygen with one or more diluents which are non-reactive with the oxygen or with the reactant or product under the conditions of reaction. Examples of such diluent gases are air, helium, argon, nitrogen, or other inert gas, or oxygen-hydrocarbon mixtures. A preferred molecular oxygen is undiluted oxygen gas.

The manner in which the solution or mixture of the N-phosphonomethyliminodiacetic acid is contacted with molecular oxygen can vary greatly. For example, the N-phosphonomethyliminodiacetic acid solution or mixture can be placed in a closed container with some free space containing molecular oxygen and shaken vigorously or agitated by stirring. Alternatively, the molecular oxygen can be continuously bubbled through the solution or mixture containing the transition metal catalyst using a straight tube or a tube with a fritted diffuser attached to it. The process of this invention only requires actively contacting the molecular oxygen-containing gas with the aqueous solution or mixture of the N-phosphonomethyliminodiacetic acid containing a transition metal catalyst.

The initial pH (pH_i) of the reaction affects the reaction rate and the selectivity to N-phosphonomethylglycine. For example, with manganese, as the initial pH increases, the reaction rate increases, but the selectivity to N-phosphonomethylglycine decreases. The pH_i of the reaction can vary widely, in the range of about 0.1 to about 7. A preferred range is about 1 to about 3 with manganese and about 0.1 to 3 with cobalt. A most preferred pH is the unadjusted pH of N-phosphonomethyliminodiacetic acid in a water solution which varies with the N-phosphonomethyliminodiacetic acid concentration and the reaction temperature.

The oxidation reaction can take place in a solution or slurry. For a solution, the initial concentration of the N-phosphonomethyliminodiacetic acid in the reaction mass is a function of the solubility of the N-phosphonomethyliminodiacetic acid in the solvent at both the desired reaction temperature and the pH_i of the solution. As the solvent temperature and pH changes, the solubility of the N-phosphonomethyliminodiacetic acid changes. A preferred initial concentration of the N-phosphonomethyliminodiacetic acid is a saturated slurry containing a solvent system at reaction conditions, which maximize the yield of N-phosphonomethylglycine in the reaction mass. A preferred concentration of N-phosphonomethyliminodiacetic acid is in the range of about 1 to 50 wt.%. It is, of course, possible to employ very dilute solutions of N-phosphonomethyliminodiacetic acid, or slurries and mixtures.

The reaction is typically carried out in an aqueous solvent. The term aqueous solvent means solutions containing at least about 50 weight % water. The preferred aqueous solvent is distilled, deionized water.

The following examples are for illustration purposes only and are not intended to limit the scope of the claimed invention.

EXAMPLES

A series of runs were made to oxidize N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine. The reactions were conducted in a modified Fisher-Porter glass pressure apparatus or an Engineer Autoclave 300 ml pressure reactor in which a stirrer was installed in the head, as were three additional valved ports that were used as a sample port, a gas inlet, and a purged gas outlet. The stirrer maintained sufficient agitation to afford thorough gas-liquid mixing. The temperature was controlled by immersing the reactor in a constant temperature oil bath. The indicated amount of transition metal catalyst was dissolved or suspended in a distilled, deionized water solution containing the indicated amount of N-phosphonomethyliminodiacetic acid. The reactor was sealed and heated to the indicated reaction temperature, then pressurized to the indicated PO₂ with oxygen gas. Agitation was initiated.

The selectivity (mole%) to N-phosphonomethylglycine was determined by dividing the moles of N-phosphonomethylglycine produced by the total moles of N-phosphonomethyliminodiacetic acid consumed and multiplying by 100. The yield (mole%) of N-phosphonomethylglycine was determined by dividing the moles of N-phosphonomethylglycine produced by the total moles of starting N-phosphonomethyliminodiacetic acid and multiplying by 100.

Examples 1 through 8

Examples 1 through 8, shown in Table 1, show the effect of varying the manganese catalyst concentration. In examples 1-4 the reaction temperature was 90° C., the PO₂ was 100 psig (690 kPa), the initial N-phosphonomethyliminodiacetic acid concentration was 0.1M. The catalyst was a mixture of Mn(II) and Mn(III) acetate salts in a 1:1 mole ratio of Mn(II) and Mn(III). Examples 5-8 were run at the same conditions as 1-4, except that the PO₂ was 450 psig (3100 kPa) and the reaction temperature was 80° C. and the catalyst was Mn(II) acetate.

TABLE 1

Effect of Varying Catalyst Concentration

Ex- am- ples	Selectivity to N-phospho- methyl- glycine (Mole %)	Manganese Concen- tration (M)	Initial Reaction Rate (Velocity, M/hr)	Yield of N-Phospho- methyl glycine (Mole %) at indi- cated time (h)
1	58	0.008	0.23	53 (6)
2	82	0.004	0.10	75 (6)
3	84	0.002	0.05	18 (14)
4	63	0.001	0.016	45 (6)
5	83	0.02	0.30	83 (8)
6	83	0.0067	0.10	81 (4)
7	70	0.004	0.07	68 (6)
8	74	0.002	0.034	68 (6)

The data indicated that the reaction rate increases with the catalyst concentration. There appeared to be a first-order dependence of the reaction rate on the catalyst concentration.

Examples 9 through 13

Examples 9 through 13, shown in Table 2, illustrate the effect of initial pH on the reaction rate and selectivity.

ity to N-phosphonomethylglycine for a manganese catalyst. The reaction temperature was 80° C., the PO₂ was 100 psig (690 kPa), the initial N-phosphonomethyliminodiacetic acid concentration was 0.1M, the reaction times are indicated and the manganese ion concentration was 0.004M. The mixture of manganese salts was the same as used in Example 1. The initial pH was adjusted using sodium hydroxide or sulfuric acid solutions. The data indicate that as the initial pH increases, the reaction rate increases, but the selectivity to N-phosphonomethylglycine decreases.

TABLE 2

Effect of Varying Initial pH				
Example	Initial pH	Initial Reaction Rate (M/h)	Yield of N-phosphonomethyl glycine (Mole %) at indicated time (h)	Selectivity to N-phosphonomethyl glycine (Mole %)(h)
9	1.20	0.0103	31 (6)	49 (6)
10	1.35	0.015	56 (5)	66 (5)
11	1.80	0.11	41 (24)	44 (24)
12	2.30	0.14	36 (24)	37 (24)
13	3.50	0.32	39 (39)	41 (1)

Examples 14 through 16

Examples 14 through 16, shown in Table 3, illustrate the effect of reaction temperature on reaction rates and selectivity to N-phosphonomethyl glycine for a manganese catalyst. The PO₂ was 450 psig, the initial N-phosphonomethyliminodiacetic acid concentration was 0.1M and the manganese ion concentration was 0.067M. The form of the manganese salt was Mn(II)SO₄ and the pH was the unadjusted pH of the acid solution.

The data indicated that as the reaction temperature increased, the reaction rate increased.

TABLE 3

Effect of Varying Temperature				
Example	Temperature (°C.)	Initial Reaction Rate (M/hr)	Selectivity to N-phosphonomethyl glycine (Mole %) at indicated time (h)	Yield of N-phosphonomethyl glycine (Mole %) at indicated time (h)
14	70	0.035	77 (5)	75 (5)
15	80	0.093	83 (14)	81 (14)
16	90	0.310	80 (8)	77 (8)

Examples 17 through 22

Examples 17 through 22, shown in Table 4, illustrate the effect of PO₂ on selectivity to N-phosphonomethylglycine for a manganese catalyst. The reaction temperature was 80° C., the initial N-phosphonomethyliminodiacetic acid concentration was 0.1, the reaction time was as indicated which allowed for almost complete conversion of the N-phosphonomethyliminodiacetic acid, and the manganese ion concentration was 0.006 M. The form of the manganese salt was Mn(II)SO₄ and the pH was the unadjusted pH of the acid solution.

The data indicated that as the PO₂ increased, the selectivity to N-phosphonomethylglycine increased.

TABLE 4

Effect of Varying PO ₂			
Example	psig (kPa)	Selectivity to N-phosphonomethyl glycine (Mole %) at the indicated time (h)	Yield of N-phosphonomethyl glycine (Mole %) at the indicated time (h)
17	40 (210)	56 (6)	54 (6)
18	70 (450)	65 (6)	63 (6)
19	100 (690)	68 (6)	66 (6)
20	130 (890)	75 (6)	73 (6)
21	225 (1550)	81 (2)	78 (2)
22	450 (3100)	83 (14)	81 (14)

Examples 23 through 29 and Control 1

Examples 23 through 29 and Control 1, shown in Table 5, illustrate the effect of varying the form of the manganese catalyst on selectivity to N-phosphonomethylglycine. The reaction temperature was 90° C., the PO₂ was 100 psig (700 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.1M, the manganese concentration was 0.004M and the reaction time was 1 h. The pH was the unadjusted pH of the acid solution.

The mN(III)chloro-(phthalocyaninato) (Control 1) was not catalytic.

TABLE 5

Effect of Varying Form of Manganese			
Example	Form	Selectivity to N-phosphonomethyl glycine (Mole %) at 1 h.	Selectivity at 6 h.
23	¹ Mn (II)/Mn (III)	43	75
24	Mn (II) acetate	18	75
25	Mn (III) acetate	20	75
26	Mn (II) sulfate	16	75
27	² Mn (II) (acac)	20	75
28	³ MnCl ₂ 4H ₂ O	82	—
29	³ MnO ₂	70	73
Control 1	⁴ Mn (III)	1	<10

¹Mn acetate, 50/50 mole ratio Mn(II)/Mn(III)

²Mn(II)bis(acetylacetonate)

³PO₂ = 450 psig (3100 kPa) at 80° C. and Mn concentration was 0.01 M.

⁴Mn(III)chloro-(phthalocyaninato)

Examples 30 through 42

Examples 30 through 42, shown in Table 6, further illustrate the present invention. The initial pH, unless otherwise indicated, was the unadjusted pH at reaction temperature, the PO₂, unless otherwise indicated, is 100 psig (690 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.1M, and the manganese catalyst was the mixture used in Example 1.

TABLE 6

Example	Run Time (h)	Catalyst Concentration (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)
30	1	.01	90	10	96
31	1	.02	80	42	97
32	1 ^a	.007	80	32	91
33	2	.01	70	8	95
34	2	.007	80	65	95
35	2 ^b	.007	70	74	96
36	2 ^c	.007	80	25	75
37	2 ^d	.007	80	22	63
38	2	.004	90	42	80
39	2	.002	90	60	75

TABLE 6-continued

Ex- am- ple	Run Time (h)	Catalyst Concentra- tion (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)
40 ^e	2½	.007	80	85	100
41 ^f	1	.007	80	95	97
42 ^g	5	.07	80	19	84

^apH = 2.3^bPO₂ = 130 psig (810 kPa)^cPO₂ = 40 psig (275 kPa)^dpH = 1.35^ePO₂ = 225 psig (1545 kPa)^fPO₂ = 450 psig (3100 kPa)^gCatalyst was Mn(II) acetylacetonate, the PO₂ was 450 psi (3000 kPa) and the initial concentration of N-phosphonomethyliminodiacetic acid was 0.5 M.

Examples 43 through 65

Examples 43 through 65, shown in Table 7, illustrate the use of cobalt catalysts in the present invention. The initial concentration of N-phosphonomethyliminodiacetic acid was 0.1 M and the catalyst was Co(II)(SO₄). The pH was the unadjusted pH of the N-phosphonomethyliminodiacetic acid of the solution, unless otherwise indicated when it was adjusted with sodium hydroxide or sulfuric acid solution.

TABLE 7

Example	Run Time (h)	Catalyst Concentration (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)	pH	PO ₂ (psi)
43	5.5	0.02	80	73	100	unadjusted	450
44	3.0	0.02	85	85	100	"	450
45	1.75	0.02	90	75	100	"	450
46	5.5	0.02	85	90	100	"	450
47	5	0.02	85	98	100	"	1000
48	2.0 ^a	0.02	85	21	31	"	450
49	5.5	0.02	85	74	98	"	300
50	3.0 ^b	0.036	90	87	100	"	450
51	4.0 ^c	0.048	80	64	97	"	450
52	5.0 ^d	0.125	85	52	99	"	450
53	18 ^e	0.5	100	16	100	6.25	100
54	18 ^e	0.5	100	28	98	1.80	100
55	18 ^e	0.5	100	16	100	2.25	100
56	18 ^e	0.5	100	0	100	4.00	100
57	18 ^e	0.5	100	35	98	1.09	100
58	18 ^e	0.5	100	9.9	22	0.77	100
59	18 ^e	0.5	100	17	98	1.7	100
60	18 ^e	0	100	0	98	9.00	100
61	18 ^e	0.01	100	20	40	0.44	100
62	2 ^f	0.01	100	28	98	1.80	100
63	2 ^g	0.01	100	26	98	1.80	100
64	18 ^h	0.01	100	26	98	1.74	100
65	5 ⁱ	0.2	85	66	99	1.7 M	450

^aThe catalyst was Co (III) (acetylacetonate)₃.^bThe initial N-phosphonomethyliminodiacetic acid concentration was 0.3 M.^cThe initial N-phosphonomethyliminodiacetic acid concentration was 0.4 M.^dThe initial N-phosphonomethyliminodiacetic acid concentration was 1.0 M.^eThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5 M, the catalyst was CoCl₂.^fThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5 M and the catalyst was Co(NO₃)₂.^gThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5 M and the catalyst was cobalt acetate.^hThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5 M and the catalyst was CoBr₂.ⁱThe initial N-phosphonomethyliminodiacetic acid concentration was 0.4 M.

Examples 66 through 85

Examples 66 through 85, shown in Table 8, illustrate iron catalysts suitable for the present invention. The PO₂ was 100 psi (690 kPa), the catalyst concentration was 0.01 M, the reaction temperature was 100° C, the run time was 18 h, and the initial concentration of the N-phosphonomethyliminodiacetic acid was 0.5M, which formed a slurry. When NaBr was added, the concentration was also 0.01 M.

TABLE 8

Example	Catalyst	Iron Catalysts		pH
		Yield (mole %)	Conversion (mole %)	
66	Fe(SO ₄) ₂	21	36	6.25
67	Fe(SO ₄) ₂	18	28	10.0
68	Fe(SO ₄) ₂	6	14	5.0
69	Fe(SO ₄) ₂ + NaBr	5	6	3.0
70	Fe(SO ₄) ₂ + NaBr	12	14	5.0
71	Fe(SO ₄) ₂ + NaBr	26	40	6.25
72	Fe(SO ₄) ₂ + NaBr	28	84	7.0
73	Fe(SO ₄) ₂ + NaBr	29	84	8.0
74	Fe(SO ₄) ₂ + NaBr	37	83	9.0
75	iron (III) (dicyano) bis (o-phenanthroline) tetrafluoroborate salt	6	12	6.25
76	iron (III) (dicyano) bis (o-phenanthroline) tetrafluoroborate salt	8	10	7.0
77	iron (III) (dicyano) bis (o-phenanthroline) tetrafluoroborate salt	3	12	9.0
78	iron (III) (dicyano) bis (o-phenanthroline) tetrafluoroborate salt	3	12	10.0
79	K ₃ Fe(CN) ₆ ^d	3	14	3.0
80	"	8	24	5.0
81	"	21	46	6.3

82	"	30	76	7.0
83	"	37	80	9.0
84	"	32	80	10.0
85	Fe(SO ₄) ₂ + Al(NO ₃) ₃	21	72	6.0

^aRun time is 8 h.

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Examples 86 through 106 and Control 2

Examples 86 through 106 and Control 2, shown in Table 9, illustrate nickel, chromium, ruthenium, aluminum, and molybdenum catalysts appropriate for the present invention. The conditions are as for those given in Table 8. The catalyst for Control 2, CuCl₂, appeared to be ineffective.

TABLE 9

Nickel Chromium, Ruthenium, Aluminum and Molybdenum Catalysts				
Examples	Catalyst	Yield (mole %)	Conversion (mole %)	pH
86	NiBr ₂	0.2	22	5.0
87	"	0.2	10	4.0
88	"	10	34	7.0
89	"	9	38	8.4
90	"	8	34	10.4
91	CrCl ₃	1	12	1.26
92	"	4	16	2.0
93	"	16	76	3.0
94	"	0.1	14	4.0
95	"	12	52	5.0
96	"	4	22	7.0
97	"	13	58	6.25

TABLE 10-continued

Vanadium Catalysts				
Examples	Catalyst	Run Time (h)	Yield (mole %)	Conversion (mole %)
109	VOSO ₄ (hydrate) ^a	5	54	91

^aThe initial concentration of N-phosphonomethyl-iminodiacetic acid was 0.15 M and the concentration of catalyst was 0.015 M.

Examples 110 and 111

Examples 110 and 111 shown in Table 11 illustrate cerium catalysts suitable for the present invention. The reaction temperature was 90° C. and the PO₂ was 130 psi (897 kPa).

TABLE 11

Cerium Catalysts						
Example	Catalyst	Run Time (h)	Catalyst Concentration (M)	N-phosphonomethyl- iminodiacetic acid Concentration (M)	Yield (mole %)	Conversion (mole %)
110	Ce(NH ₄) ₄ (SO ₄) ₄	3	0.1	1.0	7	45
111	Ce(NH ₄) ₄ (SO ₄) ₄	3	0.01	0.1	30	80

We claim:

1. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of manganese.

2. The process of claim 1 wherein the catalyst is at least one of a manganese(II), a manganese(III), or a manganese(IV) salt.

3. The process of claim 1 wherein the catalyst is selected from the group comprising manganese acetate, manganese sulfate, manganese(II)bis(acetylacetonate) and manganese chloride.

4. The process of claim 3 wherein the catalyst is a mixture of manganese(II) and manganese(III) salts.

5. The process of claim 4 wherein the salts are manganese acetate salts in a mole ratio in the range of 1:10 to 10:1.

6. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with molecular oxygen in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of manganese, wherein the reaction temperature is in the range of about 25° to 150° C., the reaction pressure is in the range of about atmospheric (101 kPa) to about 3000 psig (20,700 kPa), the partial pressure of oxygen is in the range of about 1 psig (6.9 kPa) to about 3000 psig (20,700 kPa) and the initial pH is in the range of about 0.1 to 7.0.

7. The process of claim 1 wherein the N-phosphonomethyliminodiacetic acid is present as a slurry.

* * * * *

98	RuBr ₃	70	8	6.25
99	"	18	34	10.0
100	RuBr ₂ (Me ₂ SO) ₄	34	62	6.25
101	"	25	48	11.0
102	Al(NO ₃) ₃	11	34	6.25
103	Al(NO ₃) ₃ + NaCl	12	16	6.25
Control 2	CuCl ₂	0.2	14	6.25
104	K ₄ Mo(CN) ₈	4	22	4.0
105	"	32	48	6.0
106	"	10	30	9.0

Examples 107-109

Examples 107 through 109 shown in Table 10, illustrate vanadium catalysts suitable for the present invention. The reaction temperature was 70° C., the PO₂ was 100 psi (690 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.5 M, the catalyst concentration was 0.033M.

TABLE 10

Vanadium Catalysts				
Examples	Catalyst	Run Time (h)	Yield (mole %)	Conversion (mole %)
107	VO(acetylacetonate) ₂	2	40	67
108	VOSO ₄ (hydrate)	2.25	42	94

United States Patent [19]

Riley et al.

[11] Patent Number: 4,965,402

[45] Date of Patent: Oct. 23, 1990

[54] PROCESS FOR PRODUCING
N-PHOSPHONOMETHYLGLYCINE

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[21] Appl. No.: 311,786

[22] Filed: Feb. 17, 1989

Related U.S. Application Data

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4,853,159.

[51] Int. Cl.³ C07F 9/38

[52] U.S. Cl. 562/17

[58] Field of Search 562/17

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[57] ABSTRACT

A process for producing N-phosphonomethylglycine
by the oxidation of N-phosphonomethyliminodiacetic
acid using a molecular oxygen-containing gas in the
presence of a transition metal catalyst.

7 Claims, No Drawings

PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE

This application is a division of application 5 07/112,594 filed Oct. 26, 1987, now U.S. Pat. No. 4,853,159 issued Aug. 1, 1989.

FIELD OF THE INVENTION

This invention relates to a process for producing 10 N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid using transition metal catalysts. More particularly, this invention relates to a reaction using molecular oxygen and a transition metal salt catalyst.

SUMMARY OF RELATED ART

It is known in the art that N-phosphonomethylglycine can be produced by oxidizing N-phosphonomethyliminodiacetic acid using various oxidizing methods. U.S. Pat. No. 3,950,402 discloses a method wherein N-phosphonomethyliminodiacetic acid is oxidized to N-phosphonomethylglycine in aqueous media using a free oxygen-containing gas and a heterogeneous noble metal-based catalyst such as palladium, platinum or rhodium. U.S. Pat. No. 3,954,848 discloses the oxidation of N-phosphonomethyliminodiacetic acid with hydrogen peroxide and an acid such as sulfuric or acetic acid. U.S. Pat. No. 3,969,398 discloses the oxidation of N-phosphonomethyliminodiacetic acid using molecular oxygen and a heterogeneous activated carbon catalyst. Hungarian Patent Application No. 011706 discloses the oxidation of N-phosphonomethyliminodiacetic acid with peroxide in the presence of metals or metal compounds.

R. J. Motekaitis, A. E. Martell, D. Hayes and W. W. Frenier, Can. J. Chem., 58, 1999 (1980) disclose the iron(III) or copper(II) catalyzed oxidative dealkylation of ethylene diaminetetracetic acid (EDTA) and nitrilotriacetic acid (NTA), both of which have iminodiacetic acid groups. R. J. Motekaitis, X. B. Cox, III, P. Taylor, A. E. Martell, B. Miles and T. J. Tvedt, Can. J. Chem., 60, 1207 (1982) disclose that certain metal ions, such as Ca(II), Mg(II), Fe(II), Zn(II) and Ni(II) chelate with EDTA and stabilize against oxidation, thereby reducing the rate of oxidative dealkylation.

SUMMARY OF THE INVENTION

The present invention involves a process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of a transition metal catalyst.

DETAILED DESCRIPTION OF THE INVENTION

The process of this invention involves contacting N-phosphonomethyliminodiacetic acid with a transition metal catalyst in a mixture or solution. This mixture or solution is contacted with a molecular oxygen-containing gas while heating the reaction mass to a temperature sufficiently elevated to initiate and sustain the oxidation reaction of N-phosphonomethyliminodiacetic acid to produce N-phosphonomethylglycine.

The transition metal catalyst of the present invention 65 can be any one or more of several transition metal compounds such as manganese, cobalt, iron, nickel, chromium, ruthenium, aluminum, molybdenum, vanadium

and cerium. The catalysts can be in the form of salts such as manganese salts, e.g., manganese acetate, manganese sulfate; complexes such as manganese(II)bis(acetylacetonate) (Mn(II)(acac)_2); cobalt salts such as $\text{Co(II)(SO}_4\text{)}$, $\text{Co(II)(acetylacetonate)}$, CoCl_2 , CoBr_2 , $\text{Co(NO}_3\text{)}_2$ and cobalt acetate; cerium salts such as $(\text{NH}_4)_4\text{Ce(SO}_4\text{)}_4$ and $(\text{NH}_4)_2\text{Ce(NO}_3\text{)}_6$; iron salts such as $(\text{NH}_4)_2\text{Fe(SO}_4\text{)}_2$, iron(III)(dicyano)-(bisphenanthroline) $_2$ -(tetrafluoro)borate salt and $\text{K}_3\text{Fe(CN)}_6$, and other metal salts such as NiBr_2 , CrCl_3 , $\text{RuCl}_2(\text{Me}_2\text{SO})$, RuBr_3 , $\text{Al(NO}_3\text{)}_3$, $\text{K}_4\text{Mo(CN)}_8$, $\text{VO(acetylacetonate)}_2$ and VOSO_4 . The catalyst can be added to the N-phosphonomethyliminodiacetic acid in the salt form, or a salt may be generated in situ by the addition of a source of a transition metal ion such as MnO_2 which dissolves in the reaction medium. The $\text{Mn(III)-chloro(phthalocyaninato)}$, however, is not catalytic, possibly because the phthalocyanine ligand covalently bonds to the Mn(III) and therefore inhibits the formation of N-phosphonomethyliminodiacetic acid/manganese complex in solution.

Manganese salts such as Mn(II) , Mn(III) or Mn(IV) salts can be used individually, however, the reaction displays a delayed reaction initiation time (initiation period), e.g., there is a delay before any N-phosphonomethylglycine is produced. When a mixture of Mn(II) and Mn(III) salts are used as a catalyst system, the initiation is diminished or eliminated. A preferred manganese salt catalyst is a mixture of Mn(II) and Mn(III) salts in the range of 1:10 to 10:1 mole ratio of the Mn ions. A most preferred manganese catalyst salt is a 1:1 mole ratio of Mn(II) and Mn(III) ions in the form of manganese acetate salts. A preferred cobalt catalyst is a Co(II) salt such as $\text{Co(II)(SO}_4\text{)}$, Co(II)Cl_2 , Co(II)Br_2 , Co(II)(OH)_2 and Co(II)acetate .

The concentration of the transition metal catalyst in the reaction solution can vary widely, in the range of 0.1M to 0.0001M total metal ion concentration. For manganese, the reaction appears to have a first order dependency on the catalyst concentration, e.g., the reaction rate increases linearly as the catalyst concentration increases. The preferred concentration is in the range of about 0.01M to about 0.001M, which gives a suitably fast rate of reaction that can be easily controlled and favors selectivity to N-phosphonomethylglycine.

The reaction temperature is sufficient to initiate and sustain the oxidation reaction, in the range of about 25° C to 150° C. In general, as the reaction temperature increases, the reaction rate increases. To achieve an easily controlled reaction rate and favor selectivity to N-phosphonomethylglycine, a preferred temperature range is about 50° C. to 120° C. and a most preferred is in the range of about 70° C. to 100° C. If a temperature of above about 100° C. is used, pressure will have to be maintained on the system to maintain a liquid phase.

The pressure at which this process is conducted can vary over a wide range. The range can vary from about atmospheric (101 kPa) to about 3000 psig (20700 kPa). A preferred range is about 30 psig (200 kPa) to about 1000 psig (about 6900 kPa). A most preferred range is from about 150 psig (about 1000 kPa) to 600 psig (about 4140 kPa).

The oxygen concentration, as designated by the partial pressure of oxygen (PO_2), in the reaction affects the reaction rate and the selectivity to the desired product, N-phosphonomethylglycine. As the PO_2 increases, the reaction rate generally increases and the selectivity to

N-phosphonomethylglycine increases. The PO₂ can be increased by increasing the overall reaction pressure, or by increasing the molecular oxygen concentration in the molecular oxygen-containing gas. The PO₂ can vary widely, in the range of from 1 psig (6.9 kPa) to 3000 psig (20700 kPa). A preferred range is from 30 psig (207 kPa) to 1000 psig (6900 kPa).

The term "molecular oxygen-containing gas" means molecular oxygen gas or any gaseous mixture containing molecular oxygen with one or more diluents which are non-reactive with the oxygen or with the reactant or product under the conditions of reaction. Examples of such diluent gases are air, helium, argon, nitrogen, or other inert gas, or oxygen-hydrocarbon mixtures. A preferred molecular oxygen is undiluted oxygen gas.

The manner in which the solution or mixture of the N-phosphonomethyliminodiacetic acid is contacted with molecular oxygen can vary greatly. For example, the N-phosphonomethyliminodiacetic acid solution or mixture can be placed in a closed container with some free space containing molecular oxygen and shaken vigorously or agitated by stirring. Alternatively, the molecular oxygen can be continuously bubbled through the solution or mixture containing the transition metal catalyst using a straight tube or a tube with a fritted diffuser attached to it. The process of this invention only requires actively contacting the molecular oxygen-containing gas with the aqueous solution or mixture of the N-phosphonomethyliminodiacetic acid containing a transition metal catalyst.

The initial pH (pH_i) of the reaction affects the reaction rate and the selectivity to N-phosphonomethylglycine. For example, with manganese, as the initial pH increases, the reaction rate increases, but the selectivity to N-phosphonomethylglycine decreases. The pH_i of the reaction can vary widely, in the range of about 0.1 to about 7. A preferred range is about 1 to about 3 with manganese and about 0.1 to 3 with cobalt. A most preferred pH is the unadjusted pH of N-phosphonomethyliminodiacetic acid in a water solution which varies with the N-phosphonomethyliminodiacetic acid concentration and the reaction temperature.

The oxidation reaction can take place in a solution or slurry. For a solution, the initial concentration of the N-phosphonomethyliminodiacetic acid in the reaction mass is a function of the solubility of the N-phosphonomethyliminodiacetic acid in the solvent at both the desired reaction temperature and the pH_i of the solution. As the solvent temperature and pH changes, the solubility of the N-phosphonomethyliminodiacetic acid changes. A preferred initial concentration of the N-phosphonomethyliminodiacetic acid is a saturated slurry containing a solvent system at reaction conditions, which maximize the yield of N-phosphonomethylglycine in the reaction mass. A preferred concentration of N-phosphonomethyliminodiacetic acid is in the range of about 1 to 50 wt.%. It is, of course, possible to employ very dilute solutions of N-phosphonomethyliminodiacetic acid, or slurries and mixtures.

The reaction is typically carried out in an aqueous solvent. The term aqueous solvent means solutions containing at least about 50 weight % water. The preferred aqueous solvent is distilled, deionized water.

The following examples are for illustration purposes only and are not intended to limit the scope of the claimed invention.

EXAMPLES

A series of runs were made to oxidize N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine. The reactions were conducted in a modified Fisher-Porter glass pressure apparatus or an Engineer Autoclave 300 ml pressure reactor in which a stirrer was installed in the head, as were three additional valved ports that were used as a sample port, a gas inlet, and a purged gas outlet. The stirrer maintained sufficient agitation to afford thorough gas-liquid mixing. The temperature was controlled by immersing the reactor in a constant temperature oil bath. The indicated amount of transition metal catalyst was dissolved or suspended in a distilled, deionized water solution containing the indicated amount of N-phosphonomethyliminodiacetic acid. The reactor was sealed and heated to the indicated reaction temperature, then pressurized to the indicated PO₂ with oxygen gas. Agitation was initiated.

The selectivity (mole%) to N-phosphonomethylglycine was determined by dividing the moles of N-phosphonomethylglycine produced by the total moles of N-phosphonomethyliminodiacetic acid consumed and multiplying by 100. The yield (mole%) of N-phosphonomethylglycine was determined by dividing the moles of N-phosphonomethylglycine produced by the total moles of starting M-phosphonomethyliminodiacetic acid an multiplying by 100.

Examples 1 through 8

Examples 1 through 8, shown in Table 1, show the effect of varying the manganese catalyst concentration. In examples 1-4 the reaction temperature was 90° C., the PO₂ was 100 psig (690 kPa), the initial N-phosphonomethyliminodiacetic acid concentration was 0.1M. The catalyst was a mixture of Mn(II) and Mn(III) acetate salts in a 1:1 mole ratio of Mn(II) and Mn(III). Examples 5-8 were run at the same conditions as 1-4, except that the PO₂ was 450 psig (3100 kPa) and the reaction temperature was 80° C. and the catalyst was Mn(II) acetate.

TABLE 1

Effect of Varying Catalyst Concentration				
Ex- am- ples	Selectivity to N-phospho- methyl- glycine (Mole %)	Manganese Concen- tration (M)	Initial Reaction Rate (Velocity, M/hr)	Yield of N-Phospho- methyl glycine (Mole %) at indi- cated time (h)
1	58	0.008	0.23	53 (6)
2	82	0.004	0.10	75 (6)
3	84	0.002	0.05	18 (14)
4	63	0.001	0.016	45 (6)
5	83	0.02	0.30	83 (8)
6	83	0.0067	0.10	81 (4)
7	70	0.004	0.07	68 (6)
8	74	0.002	0.034	68 (6)

The data indicated that the reaction rate increases with the catalyst concentration. There appeared to be a first-order dependence of the reaction rate on the catalyst concentration.

Examples 9 through 13

Examples 9 through 13, shown in Table 2, illustrate the effect of initial pH on the reaction rate and selectiv-

ity to N-phosphonomethylglycine for a manganese catalyst. The reaction temperature was 80° C., the PO₂ was 100 psig (690 kPa), the initial N-phosphonomethyliminodiacetic acid concentration was 0.1M, the reaction times are indicated and the manganese ion concentration was 0.004M. The mixture of manganese salts was the same as used in Example 1. The initial pH was adjusted using sodium hydroxide or sulfuric acid solutions. The data indicate that as the initial pH increases, the reaction rate increases, but the selectivity to N-phosphonomethylglycine decreases.

TABLE 2

Effect of Varying Initial pH				
Example	Initial pH	Initial Reaction Rate (M/h)	Yield of N-phosphonomethyl glycine (Mole %) at indicated time (h)	Selectivity to N-phosphonomethyl glycine (Mole %)(h)
9	1.20	0.0103	31 (6)	49 (6)
10	1.35	0.015	56 (5)	66 (5)
11	1.80	0.11	41 (24)	44 (24)
12	2.30	0.14	36 (24)	37 (24)
13	3.50	0.32	39 (39)	41 (4)

Examples 14 through 16

Examples 14 through 16, shown in Table 3, illustrate the effect of reaction temperature on reaction rates and selectivity to N-phosphonomethyl glycine for a manganese catalyst. The PO₂ was 450 psig, the initial N-phosphonomethyliminodiacetic acid concentration was 0.1M and the manganese ion concentration was 0.067M. The form of the manganese salt was Mn(II)SO₄ and the pH was the unadjusted pH of the acid solution.

The data indicated that as the reaction temperature increased, the reaction rate increased.

TABLE 3

Effect of Varying Temperature				
Example	Temperature (°C.)	Initial Reaction Rate (M/hr)	Selectivity to N-phosphonomethyl glycine (Mole %) at indicated time (h)	Yield of N-phosphonomethyl glycine (Mole %) at indicated time (h)
14	70	0.035	77 (5)	75 (5)
15	80	0.093	83 (14)	81 (14)
16	90	0.310	80 (4)	77 (4)

Examples 17 through 22

Examples 17 through 22, shown in Table 4, illustrate the effect of PO₂ on selectivity to N-phosphonomethylglycine for a manganese catalyst. The reaction temperature was 80° C., the initial N-phosphonomethyliminodiacetic acid concentration was 0.1, the reaction time was as indicated which allowed for almost complete conversion of the N-phosphonomethyliminodiacetic acid, and the manganese ion concentration was 0.006 M. The form of the manganese salt was Mn(II)SO₄ and the pH was the unadjusted pH of the acid solution.

The data indicated that as the PO₂ increased, the selectivity to N-phosphonomethylglycine increased.

TABLE 4

Effect of Varying PO ₂			
Example	psig (kPa)	Selectivity to N-phosphonomethyl glycine (Mole %) at the indicated time (h)	Yield of N-phosphonomethyl glycine (Mole %) at the indicated time (h)
17	40 (210)	56 (6)	54 (6)
18	70 (450)	65 (6)	63 (6)
19	100 (690)	68 (6)	66 (6)
20	130 (890)	75 (6)	73 (6)
21	225 (1550)	81 (2)	78 (2)
22	450 (3100)	83 (14)	81 (14)

Examples 23 through 29 and Control 1

Examples 23 through 29 and Control 1, shown in Table 5, illustrate the effect of varying the form of the manganese catalyst on selectivity to N-phosphonomethylglycine. The reaction temperature was 90° C., the PO₂ was 100 psig (700 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.1M, the manganese concentration was 0.004M and the reaction time was 1 h. The pH was the unadjusted pH of the acid solution.

The mN(III)chloro-(phthalocyaninato) (Control 1) was not catalytic.

TABLE 5

Effect of Varying Form of Manganese			
Example	Form	Selectivity to N-phosphonomethyl glycine (Mole %) at 1 h.	Selectivity at 6 h.
23	¹ Mn (II)/Mn (III)	43	75
24	Mn (II) acetate	18	75
25	Mn (III) acetate	20	75
26	Mn (II) sulfate	16	75
27	² Mn (II) (acac)	20	75
28	³ MnCl ₂ 4H ₂ O	82	—
29	³ MnO ₂	70	73
Control 1	⁴ Mn (III)	1	<10

¹Mn acetate, 50/50 mole ratio Mn(II)/Mn(III)

²Mn(II)bis(acetylacetonate)

³PO₂ = 450 psig (3100 kPa) at 80° C. and Mn concentration was 0.01 M.

⁴Mn(III)chloro-(phthalocyaninato)

Examples 30 through 42

Examples 30 through 42, shown in Table 6, further illustrate the present invention. The initial pH, unless otherwise indicated, was the unadjusted pH at reaction temperature, the PO₂, unless otherwise indicated, is 100 psig (690 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.1M, and the manganese catalyst was the mixture used in Example 1.

TABLE 6

Ex- am- ple	Run Time (h)	Catalyst Concentration (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)
30	1	.01	90	10	96
31	1	.02	80	42	97
32	1 ^a	.007	80	32	91
33	2	.01	70	8	95
34	2	.007	80	65	95
35	2 ^b	.007	70	74	96
36	2 ^c	.007	80	25	75
37	2 ^d	.007	80	22	63
38	2	.004	90	42	80
39	2	.002	90	60	75

TABLE 6-continued

Ex- am- ple	Run Time (h)	Catalyst Concentra- tion (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)
40 ^a	24	.007	80	85	100
41 ^b	1	.007	80	95	97
42 ^c	5	.07	80	19	84

^apH = 2.3^bPO₂ = 130 psig (810 kPa)^cPO₂ = 40 psig (275 kPa)^dpH = 1.35^ePO₂ = 225 psig (1545 kPa)^fPO₂ = 450 psig (3100 kPa)^gCatalyst was Mn(II) acetylacetonate, the PO₂ was 450 psi (3000 kPa) and the initial concentration of N-phosphonomethyliminodiacetic acid was 0.5 M.

Examples 43 through 65

Examples 43 through 65, shown in Table 7, illustrate the use of cobalt catalysts in the present invention. The initial concentration of N-phosphonomethyliminodiacetic acid was 0.1 M and the catalyst was Co(II)(SO₄). The pH was the unadjusted pH of the N-phosphonomethyliminodiacetic acid of the solution, unless otherwise indicated when it was adjusted with sodium hydroxide or sulfuric acid solution.

TABLE 7

Example	Run Time (h)	Catalyst Concentration (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)	pH	PO ₂ (psi)
43	5.5	0.02	80	73	100	unadjusted	450
44	3.0	0.02	85	85	100	"	450
45	1.75	0.02	90	75	100	"	450
46	5.5	0.02	85	90	100	"	450
47	5	0.02	85	98	100	"	1000
48	2.0 ^a	0.02	85	21	31	"	450
49	5.5	0.02	85	74	98	"	300
50	3.0 ^b	0.036	90	87	100	"	450
51	4.0 ^c	0.048	80	64	97	"	450
52	5.0 ^d	0.125	85	52	99	"	450
53	18 ^e	0.5	100	16	100	6.25	100
54	18 ^e	0.5	100	28	98	1.80	100
55	18 ^e	0.5	100	16	100	2.25	100
56	18 ^e	0.5	100	0	100	4.00	100
57	18 ^e	0.5	100	35	98	1.09	100
58	18 ^e	0.5	100	9.9	22	0.77	100
59	18 ^e	0.5	100	17	98	1.7	100
60	18 ^e	0	100	0	98	9.00	100
61	18 ^e	0.01	100	20	40	0.44	100
62	2 ^f	0.01	100	28	98	1.80	100
63	2 ^g	0.01	100	26	98	1.80	100
64	18 ^h	0.01	100	26	98	1.74	100
65	5 ⁱ	0.2	85	66	99	1.7 M	450

^aThe catalyst was Co (III) (acetylacetonate).^bThe initial N-phosphonomethyliminodiacetic acid concentration was 0.3 M.^cThe initial N-phosphonomethyliminodiacetic acid concentration was 0.4 M.^dThe initial N-phosphonomethyliminodiacetic acid concentration was 1.0 M.^eThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5 M, the catalyst was CoCl₂.^fThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5 M and the catalyst was Co(NO₃)₂.^gThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5 M and the catalyst was cobalt acetate.^hThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5 M and the catalyst was CoBr₂.ⁱThe initial N-phosphonomethyliminodiacetic acid concentration was 0.4 M.

Examples 66 through 85

Examples 66 through 85, shown in Table 8, illustrate iron catalysts suitable for the present invention. The PO₂ was 100 psi (690 kPa), the catalyst concentration was 0.01 M, the reaction temperature was 100° C, the run time was 18 h, and the initial concentration of the N-phosphonomethyliminodiacetic acid was 0.5M, which formed a slurry. When NaBr was added, the concentration was also 0.01 M.

TABLE 8

Iron Catalysts				
Example	Catalyst	Yield (mole %)	Conversion (mole %)	pH
66	Fe(SO ₄) ₂	21	36	6.25
67	Fe(SO ₄) ₂	18	28	10.0
68	Fe(SO ₄) ₂	6	14	5.0
69	Fe(SO ₄) ₂ + NaBr	5	6	3.0
70	Fe(SO ₄) ₂ + NaBr	12	14	5.0
71	Fe(SO ₄) ₂ + NaBr	26	40	6.25
72	Fe(SO ₄) ₂ + NaBr	28	84	7.0
73	Fe(SO ₄) ₂ + NaBr	29	84	8.0
74	Fe(SO ₄) ₂ + NaBr	37	83	9.0
75	iron (III) (dicyano) bis (o-phenanthroline) tetrafluoroborate salt	6	12	6.25
76	iron (III) (dicyano) bis (o-phenanthroline) tetrafluoroborate salt	8	10	7.0
77	iron (III) (dicyano) bis (o-phenanthroline) tetrafluoroborate salt	3	12	9.0
78	iron (III) (dicyano) bis (o-phenanthroline) tetrafluoroborate salt	3	12	10.0
79	K ₃ Fe(CN) ₆ ^a	3	14	3.0
80	"	8	24	5.0
81	"	21	46	6.3

82	"	30	76	7.0
83	"	37	80	9.0
84	"	32	80	10.0
85	Fe(SO ₄) ₂ + Al(NO ₃) ₃	21	72	6.0

^aRun time is 8 h.

Examples 86 through 106 and Control 2

Examples 86 through 106 and Control 2, shown in Table 9, illustrate nickel, chromium, ruthenium, aluminum, and molybdenum catalysts appropriate for the present invention. The conditions are as for those given in Table 8. The catalyst for Control 2, CuCl₂, appeared to be ineffective.

TABLE 9

Nickel, Chromium, Ruthenium, Aluminum and Molybdenum Catalysts				
Examples	Catalyst	Yield (mole %)	Conversion (mole %)	pH
86	NiBr ₂	0.2	22	5.0
87	"	0.2	10	4.0
88	"	10	34	7.0
89	"	9	38	8.4
90	"	8	34	10.4
91	CrCl ₃	1	12	1.26
92	"	4	16	2.0
93	"	16	76	3.0
94	"	0.1	14	4.0
95	"	12	52	5.0
96	"	4	22	7.0
97	"	13	58	6.25

TABLE 10-continued

Vanadium Catalysts				
Examples	Catalyst	Run Time (h)	Yield (mole %)	Conversion (mole %)
109	VOSO ₄ (hydrate) ^a	5	54	91

^aThe initial concentration of N-phosphonomethyliminodiacetic acid was 0.15 M and the concentration of catalyst was 0.015 M.

Examples 110 and 111

Examples 110 and 111 shown in Table 11 illustrate cerium catalysts suitable for the present invention. The reaction temperature was 90° C. and the PO₂ was 130 psi (897 kPa).

TABLE 11

Cerium Catalysts						
Example	Catalyst	Run Time (h)	Catalyst Concentration (M)	N-phosphonomethyl- iminodiacetic acid Concentration (M)	Yield (mole %)	Conversion (mole %)
110	Ce(NH ₄) ₄ (SO ₄) ₄	3	0.1	1.0	7	45
111	Ce(NH ₄) ₄ (SO ₄) ₄	3	0.01	0.1	30	80

We claim:

1. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of manganese.

2. The process of claim 1 wherein the catalyst is at least one of a manganese(II), a manganese(III), or a manganese(IV) salt.

3. The process of claim 1 wherein the catalyst is selected from the group comprising manganese acetate, manganese sulfate, manganese(II)bis(acetylacetonate) and manganese chloride.

4. The process of claim 3 wherein the catalyst is a mixture of manganese(II) and manganese(III) salts.

5. The process of claim 4 wherein the salts are manganese acetate salts in a mole ratio in the range of 1:10 to 10:1.

6. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with molecular oxygen in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of manganese, wherein the reaction temperature is in the range of about 25° to 150° C., the reaction pressure is in the range of about atmospheric (101 kPa) to about 3000 psig (20,700 kPa), the partial pressure of oxygen is in the range of about 1 psig (6.9 kPa) to about 3000 psig (20,700 kPa) and the initial pH is in the range of about 0.1 to 7.0.

7. The process of claim 1 wherein the N-phosphonomethyliminodiacetic acid is present as a slurry.

* * * * *

98	RuBr ₃	70	8	6.25
99	"	18	34	10.0
100	RuBr ₂ (Me ₂ SO) ₄	34	62	6.25
101	"	25	48	11.0
102	Al(NO ₃) ₃	11	34	6.25
103	Al(NO ₃) ₃ + NaCl	12	16	6.25
Control 2	CuCl ₂	0.2	14	6.25
104	K ₄ Mo(CN) ₈	4	22	4.0
105	"	32	48	6.0
106	"	10	30	9.0

Examples 107-109

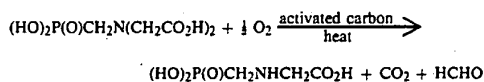
Examples 107 through 109 shown in Table 10, illustrate vanadium catalysts suitable for the present invention. The reaction temperature was 70° C., the PO₂ was 100 psi (690 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.5 M, the catalyst concentration was 0.033M.

TABLE 10

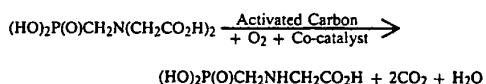
Vanadium Catalysts				
Examples	Catalyst	Run Time (h)	Yield (mole %)	Conversion (mole %)
107	VO(acetylacetonate) ₂	2	40	67
108	VOSO ₄ (hydrate)	2.25	42	94

aldehyde and formic acid readily penetrate the zeolite materials, a marked hindrance of N-phosphonomethylglycine passage can cause a large difference in rates. In addition to effects of pore size in excluding the larger molecules, diffusion factors may have a significant effect on the penetration rate, particularly in the liquid reaction systems contemplated in the present invention. While penetration rates have not been measured, the rates of formaldehyde may well be several hundred times or more greater than that of N-phosphonomethylglycine. In terms of advantage, it is desirable that the encapsulated noble metal catalyst have two or more times the life of the unencapsulated catalyst, and in fact it may ultimately be feasible for practical operation to have catalyst life many times that of the unencapsulated catalyst and sufficient to make replacement or regeneration of the noble metal catalyst a minor factor in process economics. Moreover, with regard to regeneration, it has been found that the encapsulated catalysts herein are amenable to ready regeneration by simple procedures.

The present invention is particularly concerned with a reaction to prepare N-phosphonomethylglycine by oxidative cleavage of N-phosphonomethyliminodiacetic acid,



The reaction works well, and is a suitable process for preparing N-phosphonomethylglycine. However, the formaldehyde by-product has a tendency to react further with amines, including the desired N-phosphonomethylglycine and other N-phosphonomethylamines, thereby detracting from yield of the desired product. The present invention overcomes this problem by using a co-catalyst along with the carbon, so that the formaldehyde is further oxidized to carbon dioxide and water, thereby becoming unavailable for reaction with the N-phosphonomethylglycine product, as illustrated by the following equation:



In carrying out the reaction, it is important to protect the co-catalyst from ready contact by the N-phosphonomethylamines present, as noble metal crystallite catalysts are quickly poisoned by such compounds. In the illustrated reaction showing formaldehyde as a by-product, some of the formaldehyde may be converted to formic acid which can similarly undergo interfering reactions, and in the present invention the formic acid can also be oxidized to carbon dioxide and water.

The present invention can use various noble metals for the co-catalysts, e.g., Ru, Os, Rh, Ir, Pd and Pt, with Rh or Pt generally being preferred. The amount of noble metal in the microporous support can vary widely, but will generally be in the range of above 0.1% to about 5% by weight, and amounts of about 3% or so are suitable for illustration.

In accordance with an embodiment of this invention, N-phosphonomethyliminodiacetic acid is dissolved in water and this solution contacted with a molecular oxygen-containing gas in the presence of activated car-

bon and a zeolite encapsulated co-catalyst, while heating the mixture to a temperature sufficiently elevated to cause said oxygen and said N-phosphonomethyliminodiacetic acid to react to produce N-phosphonomethylglycine.

The temperature employed in carrying out the oxidation process should be sufficient to initiate the reaction and to sustain the reaction once initiated. Temperatures of from about 25° C., to 150° C. or even higher are usually satisfactory. As those skilled in the art would realize, at lower temperatures the rate of reaction is undesirably slow and, therefore, temperatures of at least 75° C. are preferred and even more preferred are temperatures in the range of about 90° C. to 150° C. It is, of course, realized that at temperatures above about 100° C. that pressure will have to be maintained on the system to maintain a liquid phase.

The pressure at which the process to prepare N-phosphonomethylglycine is conducted can vary over wide ranges. Thus, the pressure of the molecular oxygen-containing gas can be as low as 50 kPa to 20,000 kPa or higher. It is preferred for convenience to conduct the process at a total pressure of from about 50 kPa to 20,000 kPa. It is even more preferred to conduct the process at pressures of from ambient atmospheric pressure to 700 kPa.

The manner in which the aqueous solution of the N-phosphonomethyliminodiacetic acid is contacted with the molecular oxygen-containing gas and activated carbon and co-catalyst can vary greatly. For example, the N-phosphonomethyliminodiacetic acid solution can be placed in a closed container with some free space containing molecular oxygen and shaken vigorously or agitated by stirring or the molecular oxygen-containing gas can be bubbled through said solution containing activated carbon and co-catalyst either through a straight tube or a tube with a fritted diffuser attached thereto. The contacting can also be accomplished in a tubular continuous reactor packed with activated carbon and co-catalyst. Thus, the process of this invention only requires actively contacting the molecular oxygen-containing gas with the aqueous solution of said N-phosphonomethyliminodiacetic acid containing said activated carbon catalyst and co-catalyst.

In conducting the oxidation process it is often preferred to employ approximately saturated solutions of the N-phosphonomethyliminodiacetic acid in water at the temperature of reaction for ease of reaction and ease of recovery of the product, N-phosphonomethylglycine, i.e., from about 1% by weight at 25° C., about 4% by weight at 95° C. It is, of course, possible to employ very dilute, i.e., 0.1% by weight of N-phosphonomethyliminodiacetic acid in water; however, this results in a more difficult product recovery procedure.

The reaction, of course, occurs in the aqueous phase when the solution comes in contact with the presence of the catalyst. Thus it is possible to use supersaturated solutions or slurries in which the reactant removed from solution by the oxidation reaction is replaced by the dissolution of more reactant. This maintains the amount of available reactant at a maximum and is therefore preferred to operating in a highly dilute solution.

The amount of the molecular oxygen-containing gas employed can vary over wide ranges. It is, of course, obvious to those skilled in the art that the best yields of the N-phosphonomethylglycine are produced when at least stoichiometric amounts of oxygen are employed.

In most instances for ease of reaction and best yields of the final product, N-phosphonomethylglycine, the amount of oxygen employed would ordinarily be at least $\frac{1}{2}$ mole of oxygen for each mole of N-phosphonomethyliminodiacetic acid employed. In actual practice, the amount of oxygen employed will be from $\frac{1}{2}$ to 1 or more moles for each mole of the N-phosphonomethyliminodiacetic acid employed since the efficiency of the oxygen utilization is usually less than 100%.

By the term "molecular oxygen-containing gas", as employed herein, is meant any gaseous mixture containing molecular oxygen with one or more diluents which are non-reactive with the oxygen or with the reactant or product under the conditions of reaction. Examples of such gases are air, oxygen, oxygen diluted with helium, argon, nitrogen, or other inert gas, oxygen-hydrocarbon mixtures and the like. It is preferred to employ gases containing 20 or more percent by weight molecular oxygen and even more preferred to employ gases containing 90 or more percent by weight molecular oxygen.

The activated carbon catalysts employed in the process of this invention are well known in the art and are available under a large number of trade names. These activated carbons are characterized by high adsorptive capacity for gases, vapors, various molecules dissolved in solution, and colloidal solids and relatively high specific surface areas. Carbon, char or charcoal is produced by destructive distillation of wood, peat, lignite, nut shells, bones, vegetable or other natural or synthetic carbonaceous matter, but must usually be "activated" to develop adsorptive power. Activation is usually achieved by heating to high temperatures (800°-900° C.) with steam or with carbon dioxide, which brings about a porous particle structure and increased specific surface area. In some cases hygroscopic acid or sodium sulfate, are added prior to the destructive distillation or activation, to increase adsorptive capacity. The carbon content of active carbons ranges from about 10% for bone charcoal to about 98% for some wood chars and nearly 100% for activated carbons derived from organic polymers. The non-carbonaceous matter in activated charcoal will vary depending on precursor origin and/or activation procedure. For example, inorganic "ash" components containing aluminum and silicon are oftentimes present in large amounts accompanied by certain alkali metals and alkaline earths. The later grouping influences the acidity-basicity characteristics of the activated carbon. Other inorganic constituents found in many activated carbons include iron and titanium. Depending on raw material original and activation procedure, large amounts of oxygen can be present along with lesser amounts of hydrogen, nitrogen and sulfur. Oxygen content also influences activated carbon acidity-basicity.

The specific surface area of activated carbons used herein, measured by the BET (Brunauer-Emmett-Teller) method using N_2 can range from 100 to nearly 2000 m^2/g . The packed bulk density of activated carbons will depend on the form (powder vs. particulate) and also on the measuring technique employed. Measured values less than 0.15 g/cc and as high or about 0.6 g/cc for powders have been recorded.

The amount of granular or powdered activated carbon employed in the oxidation process can range from 0.5 to 100 or more parts by weight for every 100 parts by weight of the N-phosphonomethyliminodiacetic acid

employed. For the powdered activated carbons, it is preferred to employ from 1 to 50 parts by weight of activated carbon for 100 parts by weight of the N-phosphonomethyliminodiacetic acid. For the activated carbons in granular forms, it is preferred to employ 1 to 75 parts by weight per 100 parts by weight of N-phosphonomethyliminodiacetic acid and a more prescribed range is from 20 to 60 parts by weight. It is, of course, obvious that in a tubular type reactor, hereinbefore mentioned, weight ratios of activated carbon to reactants can vary over even greater ranges than herein set forth. The amount of zeolite encapsulated catalyst can be varied as found most effective, but will generally be in the range of 2 to 15 or 20 parts by weight (metal + zeolite) per 100 parts by weight carbon catalyst, and about 5 parts is a convenient amount. The activated carbon employed can be in the form of powders or granules, and the zeolite encapsulated catalyst can be in similar form. Further description of procedures for oxidizing N-phosphonomethyliminodiacetic acid are found in Hershman U.S. Pat. No. 3,969,398, the disclosure of which is incorporated herein by reference. The activated carbons disclosed by way of example in that patent can suitably be used for the present oxidations. The encapsulated zeolite catalyst can be mixed with the carbon catalyst prior to use as a co-catalyst in a process, or it can be added to a reaction medium to which a carbon catalyst is also added, and used as a co-catalyst therein. Of course, when both catalysts are in a reaction medium, they will become admixed therein, and generally will still be mixed together when recovered from the process, or used in recycle procedures.

The amount of zeolite encapsulated catalyst can also be considered with respect to the formaldehyde or other materials to be oxidized, and the medium containing materials to be oxidized, especially in the event waste streams are being treated subsequent to a reaction. While the catalyst can be used over broad ranges of concentrations, relatively low concentrations are often effective, such as in the range of about 0.01% to 0.5% or slightly higher, of the reaction medium, with the percentages being calculated on the total weight of platinum or other noble metal and zeolite present. The percentages, of course, would be much smaller if based on the small amount of catalytic metal present and encapsulated in the zeolite.

In illustrated reactions herein, the phosphonomethyl group has been shown with a free phosphonic acid, i.e., with two -OH groups on the phosphorus. However, the present catalyst system can be usefully employed in the presence of N-phosphonomethylamines in general, including those in which the phosphono moiety is in ester or in salt form; and similarly the diacetic acid groups in the iminodiacetic acid can be in ester or salt form, with operating reactants being illustrated



in which each R is individually selected from hydrogen, or salt or ester forming groups. Exemplifications of suitable ester forming groups are hydrocarbyl groups, particularly short-chain alkyl groups such as methyl and ethyl groups. Alkali metal, e.g., sodium or potassium, alkaline earth metal and ammonium salts can conveniently be used. The oxidation reaction is conveniently conducted in water, but other solvents can be employed, e.g., glacial acetic acid, aqueous acetic acid, or various other solvents which are resistant to oxida-



US005091561A

United States Patent [19]

Riley et al.

[11] **Patent Number:** 5,091,561[45] **Date of Patent:** Feb. 25, 1992[54] **PROCESS FOR PRODUCING
N-PHOSPHONOMETHYLGLYCINE**[75] **Inventors:** Dennis P. Riley, Chesterfield; Willie
J. Rivers, Jr., University City, both
of Mo.[73] **Assignee:** Monsanto Company, St. Louis, Mo.[21] **Appl. No.:** 532,413[22] **Filed:** Jun. 4, 1990**Related U.S. Application Data**[62] Division of Ser. No. 311,786, Feb. 17, 1989, Pat. No.
4,965,402, which is a division of Ser. No. 112,594, Oct.
26, 1987, Pat. No. 4,853,159.[51] **Int. Cl.⁵** C07F 9/38[52] **U.S. Cl.** 562/17[58] **Field of Search** 562/17[56] **References Cited****U.S. PATENT DOCUMENTS**3,969,398 7/1976 Herschman 562/17
4,696,772 9/1987 Chou 562/17**FOREIGN PATENT DOCUMENTS**

2049697 12/1980 United Kingdom 562/17

OTHER PUBLICATIONSMotekaitis et al (I), Can. J. Chem. 58 1999 (1980).
Motekaitis et al. (II), Can. J. Chem., 60 1207 (1982).*Primary Examiner*—J. E. Evans*Attorney, Agent, or Firm*—Frank D. Shearin[57] **ABSTRACT**A process for producing N-phosphonomethylglycine
by the oxidation of N-phosphonomethyliminodiacetic
acid using a molecular oxygen-containing gas in the
presence of a transition metal catalyst.**16 Claims, No Drawings**

PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a division of application Ser. No. 07/311,786 filed Feb. 17, 1989, now U.S. Pat. No. 4,965,402, which is a division of application Ser. No. 07/112,594 filed Oct. 26, 1987, now U.S. Pat. No. 4,853,159 issued Aug. 1, 1989.

FIELD OF THE INVENTION

This invention relates to a process for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid using transition metal catalysts. More particularly, this invention relates to a reaction using molecular oxygen and a transition metal salt catalyst.

SUMMARY OF RELATED ART

It is known in the art that N-phosphonomethylglycine can be produced by oxidizing N-phosphonomethyliminodiacetic acid using various oxidizing methods. U.S. Pat. No. 3,950,402 discloses a method wherein N-phosphonomethyliminodiacetic acid is oxidized to N-phosphonomethylglycine in aqueous media using a free oxygen-containing gas and a heterogeneous noble metal-based catalyst such as palladium, platinum or rhodium. U.S. Pat. No. 3,954,848 discloses the oxidation of N-phosphonomethyliminodiacetic acid with hydrogen peroxide and an acid such as sulfuric or acetic acid. U.S. Pat. No. 3,969,398 discloses the oxidation of N-phosphonomethyliminodiacetic acid using molecular oxygen and a heterogeneous activated carbon catalyst. Hungarian Patent Application No. 011706 discloses the oxidation of N-phosphonomethyliminodiacetic acid with peroxide in the presence of metals or metal compounds.

R. J. Motekaitis, A. E. Martell, D. Hayes and W. W. Frenier, *Can. J. Chem.*, 58, 1999 (1980) disclose the iron(III) or copper(II) catalyzed oxidative dealkylation of ethylene diaminetetracetic acid (EDTA) and nitrilotriacetic acid (NTA), both of which have iminodiacetic acid groups. R. J. Motekaitis, X. B. Cox, III, P. Taylor, A. E. Martell, B. Miles and T. J. Tvedt, *Can. J. Chem.*, 60, 1207 (1982) disclose that certain metal ions, such as Ca(II), Mg(II), Fe(II), Zn(II) and Ni(II) chelate with EDTA and stabilize against oxidation, thereby reducing the rate of oxidative dealkylation.

SUMMARY OF THE INVENTION

The present invention involves a process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of a transition metal catalyst.

DETAILED DESCRIPTION OF THE INVENTION

The process of this invention involves contacting N-phosphonomethyliminodiacetic acid with a transition metal catalyst in a mixture or solution. This mixture or solution is contacted with a molecular oxygen-containing gas while heating the reaction mass to a temperature sufficiently elevated to initiate and sustain the oxidation

reaction of N-phosphonomethyliminodiacetic acid to produce N-phosphonomethylglycine.

The transition metal catalyst of the present invention can be any one or more of several transition metal compounds such as manganese, cobalt, iron, nickel, chromium, ruthenium, aluminum, molybdenum, vanadium and cerium. The catalysts can be in the form of salts such as manganese salts, e.g., manganese acetate, manganese sulfate; complexes such as manganese(II)bis(acetylacetonate) (Mn(II)(acac)_2); cobalt salts such as $\text{Co(II)(SO}_4\text{)}$, $\text{Co(II)(acetylacetonate)}$, CoCl_2 , CoBr_2 , $\text{Co(NO}_3\text{)}_2$ and cobalt acetate; cerium salts such as $(\text{NH}_4)_4\text{Ce(SO}_4\text{)}_6$ and $(\text{NH}_4)_2\text{Ce(NO}_3\text{)}_6$; iron salts such as $(\text{NH}_4)_2\text{Fe(SO}_4\text{)}_2$, iron(III) (dicyano) (bisphenanthroline) $_2$ -(tetrafluoroborate) salt and $\text{K}_3\text{Fe(CN)}_6$, and other metal salts such as NiBr_2 , CrCl_3 , $\text{RuCl}_2(\text{Me}_2\text{SO})$, RuBr_3 , $\text{Al(NO}_3\text{)}_3$, $\text{K}_4\text{Mo(CN)}_8$, $\text{VO(acetylacetonate)}_2$ and VOSO_4 . The catalyst can be added to the N-phosphonomethyliminodiacetic acid in the salt form, or a salt may be generated in situ by the addition of a source of a transition metal ion such as MnO_2 which dissolves in the reaction medium. The Mn(II)-chloro(phthalocyaninato), however, is not catalytic, possibly because the phthalocyanine ligand covalently bonds to the Mn(III) and therefore inhibits the formation of N-phosphonomethyliminodiacetic acid/manganese complex in solution.

Manganese salts such as Mn(II), Mn(III) or Mn(IV) salts can be used individually, however, the reaction displays a delayed reaction initiation time (initiation period), e.g., there is a delay before any N-phosphonomethylglycine is produced. When a mixture of Mn(II) and Mn(III) salts are used as a catalyst system, the initiation is diminished or eliminated. A preferred manganese salt catalyst is a mixture of Mn(II) and Mn(III) salts in the range of 1:10 to 10:1 mole ratio of the Mn ions. A most preferred manganese catalyst salt is a 1:1 mole ratio of Mn(II) and Mn(III) ions in the form of manganese acetate salts. A preferred cobalt catalyst is a Co(II) salt such as $\text{Co(II)(SO}_4\text{)}$, Co(II)Cl_2 , Co(II)Br_2 , Co(II)(OH)_2 and Co(II)acetate .

The concentration of the transition metal catalyst in the reaction solution can vary widely, in the range of 0.1 M to 0.0001 M total metal ion concentration. For manganese, the reaction appears to have a first order dependency on the catalyst concentration, e.g., the reaction rate increases linearly as the catalyst concentration increases. The preferred concentration is in the range of about 0.01 M to about 0.001 M, which gives a suitably fast rate of reaction that can be easily controlled and favors selectivity to N-phosphonomethylglycine.

The reaction temperature is sufficient to initiate and sustain the oxidation reaction, in the range of about 25° C. to 150° C. In general, as the reaction temperature increases, the reaction rate increases. To achieve an easily controlled reaction rate and favor selectivity to N-phosphonomethylglycine, a preferred temperature range is about 50° C. to 120° C. and a most preferred is in the range of about 70° C. to 100° C. If a temperature of above about 100° C. is used, pressure will have to be maintained on the system to maintain a liquid phase.

The pressure at which this process is conducted can vary over a wide range. The range can vary from about atmospheric (101 kPa) to about 3000 psig (20700 kPa). A preferred range is about 30 psig (200 kPa) to about 1000 psig (about 6900 kPa). A most preferred range is

from about 150 psig (about 1000 kPa) to 600 psig (about 4140 kPa).

The oxygen concentration, as designated by the partial pressure of oxygen (PO_2), in the reaction affects the reaction rate and the selectivity to the desired product, N-phosphonomethylglycine. As the PO_2 increases, the reaction rate generally increases and the selectivity to N-phosphonomethylglycine increases. The PO_2 can be increased by increasing the overall reaction pressure, or by increasing the molecular oxygen concentration in the molecular oxygen-containing gas. The PO_2 can vary widely, in the range of from 1 psig (6.9 kPa) to 3000 psig (20700 kPa). A preferred range is from 30 psig (207 kPa) to 1000 psig (6900 kPa).

The term "molecular oxygen-containing gas" means molecular oxygen gas or any gaseous mixture containing molecular oxygen with one or more diluents which are non-reactive with the oxygen or with the reactant or product under the conditions of reaction. Examples of such diluent gases are air, helium, argon, nitrogen, or other inert gas, or oxygen-hydrocarbon mixtures. A preferred molecular oxygen is undiluted oxygen gas.

The manner in which the solution or mixture of the N-phosphonomethyliminodiacetic acid is contacted with molecular oxygen can vary greatly. For example, the N-phosphonomethyliminodiacetic acid solution or mixture can be placed in a closed container with some free space containing molecular oxygen and shaken vigorously or agitated by stirring. Alternatively, the molecular oxygen can be continuously bubbled through the solution or mixture containing the transition metal catalyst using a straight tube or a tube with a fritted diffuser attached to it. The process of this invention only requires actively contacting the molecular oxygen containing gas with the aqueous solution or mixture of the N-phosphonomethyliminodiacetic acid containing a transition metal catalyst.

The initial pH (pHi) of the reaction affects the reaction rate and the selectivity to N-phosphonomethylglycine. For example, with manganese, as the initial pH increases, the reaction rate increases, but the selectivity to N-phosphonomethylglycine decreases. The pHi of the reaction can vary widely, in the range of about 0.1 to about 7. A preferred range is about 1 to about 3 with manganese and about 0.1 to 3 with cobalt. A most preferred pH is the unadjusted pH of N-phosphonomethyliminodiacetic acid in a water solution which varies with the N-phosphonomethyliminodiacetic acid concentration and the reaction temperature.

The oxidation reaction can take place in a solution or slurry. For a solution, the initial concentration of the N-phosphonomethyliminodiacetic acid in the reaction mass is a function of the solubility of the N-phosphonomethyliminodiacetic acid in the solvent at both the desired reaction temperature and the pHi of the solution. As the solvent temperature and pH changes, the solubility of the N-phosphonomethyliminodiacetic acid changes. A preferred initial concentration of the N-phosphonomethyliminodiacetic acid is a saturated slurry containing a solvent system at reaction conditions, which maximize the yield of N-phosphonomethylglycine in the reaction mass. A preferred concentration of N-phosphonomethyliminodiacetic acid is in the range of about 1 to 50 wt. %. It is, of course, possible to employ very dilute solutions of N-phosphonomethyliminodiacetic acid, or slurries and mixtures.

The reaction is typically carried out in an aqueous solvent. The term aqueous solvent means solutions con-

taining at least about 50 weight % water. The preferred aqueous solvent is distilled, deionized water.

The following examples are for illustration purposes only and are not intended to limit the scope of the claimed invention.

EXAMPLES

A series of runs were made to oxidize N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine. The reactions were conducted in a modified Fisher-Porter glass pressure apparatus or an Engineer Autoclave 300 ml pressure reactor in which a stirrer was installed in the head, as were three additional valved ports that were used as a sample port, a gas inlet, and a purged gas outlet. The stirrer maintained sufficient agitation to afford thorough gas-liquid mixing. The temperature was controlled by immersing the reactor in a constant temperature oil bath. The indicated amount of transition metal catalyst was dissolved or suspended in a distilled, deionized water solution containing the indicated amount of N-phosphonomethyliminodiacetic acid. The reactor was sealed and heated to the indicated reaction temperature, then pressurized to the indicated PO_2 with oxygen gas. Agitation was initiated.

The selectivity (mole %) to N-phosphonomethylglycine was determined by dividing the moles of N-phosphonomethylglycine produced by the total moles of N-phosphonomethyliminodiacetic acid consumed and multiplying by 100. The yield (mole %) of N-phosphonomethylglycine was determined by dividing the moles of N-phosphonomethylglycine produced by the total moles of starting N-phosphonomethyliminodiacetic acid and multiplying by 100.

EXAMPLES 1 THROUGH 8

Examples 1 through 8, shown in Table 1, show the effect of varying the manganese catalyst concentration. In examples 1-4 the reaction temperature was 90° C., the PO_2 was 100 psig (690 kPa), the initial N-phosphonomethyliminodiacetic acid concentration was 0.1 M. The catalyst was a mixture of Mn(II) and Mn(III) acetate salts in a 1:1 mole ratio of Mn(II) and Mn(III). Examples 5-8 were run at the same conditions as 1-4, except that the PO_2 was 450 psig (3100 kPa) and the reaction temperature was 80° C. and the catalyst was Mn(II) acetate.

TABLE 1

Effect of Varying Catalyst Concentration

Ex- am- ples	Selectivity to N-phospho- methyl- glycine (Mole %)	Manga- nese Concen- tration (M)	Initial Reaction Rate (Velocity, M/hr)	Yield of N-Phosphono- methyl glycine (Mole %) at indi- cated time (h)
1	58	0.008	0.23	53(6)
2	82	0.004	0.10	75(6)
3	84	0.002	0.05	18(14)
4	63	0.001	0.016	45(6)
5	83	0.02	0.30	83(1)
6	83	0.0067	0.10	81(1)
7	70	0.004	0.07	68(6)
8	74	0.002	0.034	68(6)

The data indicated that the reaction rate increases with the catalyst concentration. There appeared to be a

first-order dependence of the reaction rate on the catalyst concentration.

EXAMPLES 9 THROUGH 13

Examples 9 through 13, shown in Table 2, illustrate the effect of initial pH on the reaction rate and selectivity to N-phosphonomethylglycine for a manganese catalyst. The reaction temperature was 80° C., the PO₂ was 100 psig (690 kPa), the initial N-phosphonomethyliminodiacetic acid concentration was 0.1 M, the reaction times are indicated and the manganese ion concentration was 0.004 M. The mixture of manganese salts was the same as used in Example 1. The initial pH was adjusted using sodium hydroxide or sulfuric acid solutions. The data indicate that as the initial pH increases, the reaction rate increases, but the selectivity to N-phosphonomethylglycine decreases.

TABLE 2

Effect of Varying Initial pH				
Example	Initial pH	Initial Reaction Rate (M/h)	Yield of N-phosphonomethylglycine (Mole %) at indicated time (h)	Selectivity to N-phosphonomethylglycine (Mole %)(h)
9	1.20	0.0103	31(6)	49(6)
10	1.35	0.015	56(5)	66(5)
11	1.80	0.11	41(24)	44(24)
12	2.30	0.14	36(24)	37(24)
13	3.50	0.32	39(39)	41(4)

EXAMPLES 14 THROUGH 16

Examples 14 through 16, shown in Table 3, illustrate the effect of reaction temperature on reaction rates and selectivity to N-phosphonomethylglycine for a manganese catalyst. The PO₂ was 450 psig, the initial N-phosphonomethyliminodiacetic acid concentration was 0.1 M and the manganese ion concentration was 0.067 M. The form of the manganese salt was Mn(II)SO₄ and the pH was the unadjusted pH of the acid solution.

The data indicated that as the reaction temperature increased, the reaction rate increased.

TABLE 3

Effect of Varying Temperature				
Example	Temperature (°C.)	Initial Reaction Rate (M/hr)	Selectivity to N-phosphonomethylglycine (Mole %) at indicated time (h)	Yield of N-phosphonomethylglycine (Mole %) at indicated time (h)
14	70	0.035	77 (5)	75(5)
15	80	0.093	83 (14)	81(14)
16	90	0.310	80 (4)	77(4)

EXAMPLES 17 THROUGH 22

Examples 17 through 22, shown in Table 4, illustrate the effect of PO₂ on selectivity to N-phosphonomethylglycine for a manganese catalyst. The reaction temperature was 80° C., the initial N-phosphonomethyliminodiacetic acid concentration was 0.1, the reaction time was as indicated which allowed for almost complete conversion for the N-phosphonomethyliminodiacetic acid, and the manganese ion concentration was 0.006 M. The form of the manganese salt was Mn(II)SO₄ and the pH was the unadjusted pH of the acid solution.

The data indicated that as the PO₂ increased, the selectivity to N-phosphonomethylglycine increased.

TABLE 4

Effect of Varying PO ₂			
Example	PO ₂ psig (kPa)	Selectivity to N-phosphonomethylglycine (Mole %) at the indicated time (h)	Yield of N-phosphonomethylglycine (Mole %) at the indicated time (h)
17	40(210)	56(6)	54(6)
18	70(450)	65(6)	63(6)
19	100(690)	68(6)	66(6)
20	130(890)	75(6)	73(6)
21	225(1550)	81(2)	78(2)
22	450(3100)	83(14)	81(14)

EXAMPLES 23 THROUGH 29

AND CONTROL 1

Examples 23 through 29 and Control 1, shown in Table 5, illustrate the effect of varying the form of the manganese catalyst on selectivity to N-phosphonomethylglycine. The reaction temperature was 90° C., the PO₂ was 100 psig (700 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.1 M, the manganese concentration was 0.004 M and the reaction time was 1 h. The pH was the unadjusted pH of the acid solution.

The Mn(III)chloro-(phthalocyaninato) (Control 1) was not catalytic.

TABLE 5

Effect of Varying Form of Manganese			
Example	Form	Selectivity to N-phosphonomethylglycine (Mole %) at 1 h.	Selectivity at 6 h.
23	¹ Mn(II)/Mn(III)	43	75
24	Mn(II)acetate	18	75
25	Mn(III)acetate	20	75
26	Mn(II)sulfate	16	75
27	² Mn(II)(acac)	20	75
28	³ MnCl ₂ 4H ₂ O	82	—
29	⁴ MnO ₂	70	73
Control 1	⁴ Mn(III)	1	<10

¹Mn acetate, 50/50 mole ratio Mn(II)/Mn(III)

²Mn(II)bis(acetylacetonate)

³PO₂ = 450 psig (3100 kPa) at 80° C. and Mn concentration was 0.01M.

⁴Mn(III)chloro-(phthalocyaninato)

EXAMPLES 30 THROUGH 42

Examples 30 through 42, shown in Table 6, further illustrate the present invention. The initial pH, unless otherwise indicated, was the unadjusted pH at reaction temperature, the PO₂, unless otherwise indicated, is 100 psig (690 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.1 M, and the manganese catalyst was the mixture used in Example 1.

TABLE 6

Ex-ample	Run Time (h)	Catalyst Concentration (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)
30	1	.01	90	10	96
31	1	.02	80	42	97
32	1 ^a	.007	80	32	91
33	2	.01	70	8	95

TABLE 6-continued

Ex-ample	Run Time (h)	Catalyst Concentration (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)
34	2	.007	80	65	95
35	2 ^b	.007	70	74	96
36	2 ^c	.007	80	25	75
37	2 ^d	.007	80	22	63
38	2	.004	90	42	80
39	2	.002	90	60	75
40 ^e	2½	.007	80	85	100
41 ^f	1	.007	80	95	97
42 ^g	5	.07	80	19	84

^apH = 2.3^bPO₂ = 130 psig (810 kPa)^cPO₂ = 40 psig (275 kPa)^dpH = 1.35^ePO₂ = 225 psig (1545 kPa)^fPO₂ = 450 psig (3100 kPa)^gCatalyst was Mn(II)acetylacetonate, the PO₂ was 450 psi (3000 kPa) and the initial concentration of N-phosphonomethyliminodiacetic acid was 0.5M.

EXAMPLES 43 THROUGH 65

Examples 43 through 65, shown in Table 7, illustrate the use of cobalt catalysts in the present invention. The initial concentration of N-phosphonomethyliminodiacetic acid was 0.1 M and the catalyst was Co(II)(SO₄). The pH was the unadjusted pH of the N-phosphonomethyliminodiacetic acid of the solution, unless otherwise indicated when it was adjusted with sodium hydroxide or sulfuric acid solution.

TABLE 7

Cobalt Catalysts							
Example	Run Time (h)	Catalyst Concentration (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)	pH	PO ₂ (psi)
43	5.5	0.02	80	73	100	unadjusted	450
44	3.0	0.02	85	85	100	unadjusted	450
45	1.75	0.02	90	75	100	unadjusted	450
46	5.5	0.02	85	90	100	unadjusted	450
47	5	0.02	85	98	100	unadjusted	1000
48	2.0 ^a	0.02	85	21	31	unadjusted	450
49	5.5	0.02	85	74	98	unadjusted	300
50	3.0 ^b	0.036	90	87	100	unadjusted	450
51	4.0 ^c	0.048	80	64	97	unadjusted	450
52	5.0 ^d	0.125	85	52	99	unadjusted	450
53	18 ^e	0.5	100	16	100	6.25	100
54	18 ^e	0.5	100	28	98	1.80	100
55	18 ^e	0.5	100	16	100	2.25	100
56	18 ^e	0.5	100	0	100	4.00	100
57	18 ^e	0.5	100	35	98	1.09	100
58	18 ^e	0.5	100	9.9	22	0.77	100
59	18 ^e	0.5	100	17	98	1.7	100
60	18 ^e	0	100	0	98	9.00	100
61	18 ^e	0.01	100	20	40	0.44	100
62	2 ^f	0.01	100	28	98	1.80	100
63	2 ^g	0.01	100	26	98	1.80	100
64	18 ^h	0.01	100	26	98	1.74	100
65	5 ⁱ	0.2	85	66	99	1.7M	450

^aThe catalyst was Co(III)(acetylacetonate).^bThe initial N-phosphonomethyliminodiacetic acid concentration was 0.3M.^cThe initial N-phosphonomethyliminodiacetic acid concentration was 0.4M.^dThe initial N-phosphonomethyliminodiacetic acid concentration was 1.0M.^eThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5M, the catalyst was CoCl₂.^fThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5M and the catalyst was Co(NO₃)₂.^gThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5M and the catalyst was cobalt acetate.^hThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5M and the catalyst was CoBr₂.ⁱThe initial N-phosphonomethyliminodiacetic acid concentration was 0.4M.

EXAMPLES 66 THROUGH 85

Examples 66 through 85, shown in Table 8, illustrate iron catalysts suitable for the present invention. The 65 PO₂ was 100 psi (690 kPa), the catalyst concentration was 0.01 M, the reaction temperature was 100° C., the run time was 18 h, and the initial concentration of the

N-phosphonomethyliminodiacetic acid was 0.5 M, which formed a slurry. When NaBr was added, the concentration was also 0.01 M.

TABLE 8

Iron Catalysts				
Example	Catalyst	Yield (mole %)	Conversion (mole %)	pH
66	Fe(SO ₄) ₂	21	36	6.25
67	Fe(SO ₄) ₂	18	28	10.0
68	Fe(SO ₄) ₂	6	14	5.0
69	Fe(SO ₄) ₂ + NaBr	5	6	3.0
70	Fe(SO ₄) ₂ + NaBr	12	14	5.0
71	Fe(SO ₄) ₂ + NaBr	26	40	6.25
72	Fe(SO ₄) ₂ + NaBr	28	84	7.0
73	Fe(SO ₄) ₂ + NaBr	29	84	8.0
74	Fe(SO ₄) ₂ + NaBr	37	83	9.0
75	iron(III)(dicyano)bis (o-phenanthroline) tetra-fluoroborate salt	6	12	6.25
76	iron(III)(dicyano)bis (o-phenanthroline) tetra-fluoroborate salt	8	10	7.0
77	iron(III)(dicyano)bis (o-phenanthroline) tetra-fluoroborate salt	3	12	9.0
78	iron(III)(dicyano)bis (o-phenanthroline) tetra-fluoroborate salt	3	12	10.0
79	K ₃ Fe(CN) ₆ ^a	3	14	3.0
80	K ₃ Fe(CN) ₆ ^a	8	24	5.0
81	K ₃ Fe(CN) ₆ ^a	21	46	6.3
82	K ₃ Fe(CN) ₆ ^a	30	76	7.0
83	K ₃ Fe(CN) ₆ ^a	37	80	9.0
84	K ₃ Fe(CN) ₆ ^a	32	80	10.0

85 Fe(SO₄)₂ + Al(NO₃)₃ 21 72 6.0^aRun time is 8 h.

EXAMPLES 86 THROUGH 106 AND CONTROL 2

Examples 86 through 106 and Control 2, shown in Table 9, illustrate nickel, chromium, ruthenium, aluminum, and molybdenum catalysts appropriate for the present invention. The conditions are as for those given in Table 8. The catalyst for Control 2, CuCl_2 , appeared to be ineffective.

TABLE 9

Nickel Chromium, Ruthenium, Aluminum and Molybdenum Catalysts				
Examples	Catalyst	Yield (mole %)	Conversion (mole %)	pH
86	NiBr_2	0.2	22	5.0
87	NiBr_2	0.2	10	4.0
88	NiBr_2	10	34	7.0
89	NiBr_2	9	38	8.4
90	NiBr_2	8	34	10.4
91	CrCl_3	1	12	1.26
92	CrCl_3	4	16	2.0
93	CrCl_3	16	76	3.0
94	CrCl_3	0.1	14	4.0
95	CrCl_3	12	52	5.0
96	CrCl_3	4	22	7.0
97	CrCl_3	13	58	6.25
98	RuBr_3	70	8	6.25
99	RuBr_3	18	34	10.0
100	$\text{RuBr}_2(\text{Me}_2\text{SO})_4$	34	62	6.25
101	$\text{RuBr}_2(\text{Me}_2\text{SO})_4$	25	48	11.0
102	$\text{Al}(\text{NO}_3)_3$	11	34	6.25
103	$\text{Al}(\text{NO}_3)_3 + \text{NaCl}$	12	16	6.25
Control 2	CuCl_2	0.2	14	6.25
104	$\text{K}_4\text{Mo}(\text{CN})_8$	4	22	4.0
105	$\text{K}_4\text{Mo}(\text{CN})_8$	32	48	6.0
106	$\text{K}_4\text{Mo}(\text{CN})_8$	10	30	9.0

EXAMPLES 107-109

Examples 107 through 109 shown in Table 10, illustrate vanadium catalysts suitable for the present invention. The reaction temperature was 70° C., the PO_2 was 100 psi (690 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.5 M, the catalyst concentration was 0.033 M.

TABLE 10

Vanadium Catalysts				
Examples	Catalyst	Run Time (h)	Yield (mole %)	Conversion (mole %)
107	$\text{VO}(\text{acetylacetonate})_2$	2	40	67
108	$\text{VO}\text{SO}_4(\text{hydrate})$	2.25	42	94
109	$\text{VO}\text{SO}_4(\text{hydrate})^a$	5	54	91

^aThe initial concentration of N-phosphonomethyliminodiacetic acid was 0.15M and the concentration of catalyst was 0.015M.

EXAMPLES 110 AND 111

Examples 110 and 111 shown in Table 11 illustrate cerium catalysts suitable for the present invention. The reaction temperature was 90° C. and the PO_2 was 130 psi (897 kPa).

TABLE 11

Cerium Catalysts						
Example	Catalyst	Run Time (h)	Catalyst Concentration (M)	N-phosphonomethyliminodiacetic acid Concentration (M)	Yield (mole %)	Conversion (mole %)
110	$\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4$	3	0.1	1.0	7	45
111	$\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4$	3	0.01	0.1	30	80

We claim:

1. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of iron, nickel, chromium, ruthenium, aluminum, molybdenum, vanadium and cerium.

2. The process of claim 1 wherein the catalyst is at least one of an iron(III), a nickel(II), a chromium(III), a ruthenium(II), a ruthenium(III), an aluminum(III), a molybdenum(IV), a molybdenum(V), a molybdenum(VI), a vanadium(IV), a vanadium(V), a cerium(III) and a cerium(IV) salt.

3. The process of claim 1 wherein the catalyst is selected from the group consisting of iron(III) diammonium disulfate, vanadiumoxy (acetylacetonate), and vanadiumoxysulfate (hydrate).

4. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with molecular oxygen in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of vanadium and cerium, wherein the reaction temperature is in the range of about 25° C. to 150° C., the reaction pressure is in the range of about atmospheric (101 kPa) to about 3000 psig (20,700 kPa), the partial pressure of oxygen is in the range of about 1 psig (6.9 kPa) to about 3000 psig (20,700 kPa) and the initial pH is in the range of about 0.1 to 7.0.

5. The process of claim 1 wherein the catalyst is at least one of a vanadium(IV), a vanadium(V), a cerium(III) and a cerium(IV) salt.

6. The process of claim 1 wherein the N-phosphonomethyliminodiacetic acid is present as a slurry.

7. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of iron, nickel and ruthenium.

8. The process of claim 7 wherein the catalyst is at least one of an iron(III), a nickel(II), a ruthenium(II), or a ruthenium(III) salt.

9. The process of claim 7 wherein the catalyst is iron(III) diammonium disulfate.

10. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of iron and nickel.

11. The process of claim 10 wherein the catalyst is at least one of an iron(III) or a nickel(II) salt.

12. The process of claim 10 wherein the catalyst is iron(III) diammonium disulfate.

13. The process of claim 7 or 10 wherein the N-phosphonomethyliminodiacetic acid is present as a slurry.

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14. A process for the production of N-phosphonome-
thylglycine comprising contacting N-phosphonome-
thyliminodiacetic acid with a molecular oxygen-con-
taining gas in the presence of an aqueous soluble cata-

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lyst selected from the group consisting of the salts and
salt complexes of nickel.

15. The process of claim 14 wherein the catalyst is a
nickel(II) salt.

16. The process of claim 14 wherein the N-phos-
phonomethyliminodiacetic acid is present as a slurry.

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United States Patent [19]

Riley et al.

[11] Patent Number: 5,091,561

[45] Date of Patent: Feb. 25, 1992

**[54] PROCESS FOR PRODUCING
N-PHOSPHONOMETHYLGLYCINE**

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[73] Assignee: Monsanto Company, St. Louis, Mo.

[21] Appl. No.: 532,413

[22] Filed: Jun. 4, 1990

Related U.S. Application Data

[62] Division of Ser. No. 311,786, Feb. 17, 1989, Pat. No. 4,965,402, which is a division of Ser. No. 112,594, Oct. 26, 1987, Pat. No. 4,853,159.

[51] Int. Cl.³ C07F 9/38

[52] U.S. Cl. 562/17

[58] Field of Search 562/17

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[57] ABSTRACT

A process for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid using a molecular oxygen-containing gas in the presence of a transition metal catalyst.

16 Claims, No Drawings

PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE

CROSS REFERENCE TO RELATED APPLICATIONS

This application is a division of application Ser. No. 07/311,786 filed Feb. 17, 1989, now U.S. Pat. No. 4,965,402, which is a division of application Ser. No. 07/112,594 filed Oct. 26, 1987, now U.S. Pat. No. 4,853,159 issued Aug. 1, 1989.

FIELD OF THE INVENTION

This invention relates to a process for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid using transition metal catalysts. More particularly, this invention relates to a reaction using molecular oxygen and a transition metal salt catalyst.

SUMMARY OF RELATED ART

It is known in the art that N-phosphonomethylglycine can be produced by oxidizing N-phosphonomethyliminodiacetic acid using various oxidizing methods. U.S. Pat. No. 3,950,402 discloses a method wherein N-phosphonomethyliminodiacetic acid is oxidized to N-phosphonomethylglycine in aqueous media using a free oxygen-containing gas and a heterogeneous noble metal-based catalyst such as palladium, platinum or rhodium. U.S. Pat. No. 3,954,848 discloses the oxidation of N-phosphonomethyliminodiacetic acid with hydrogen peroxide and an acid such as sulfuric or acetic acid. U.S. Pat. No. 3,969,398 discloses the oxidation of N-phosphonomethyliminodiacetic acid using molecular oxygen and a heterogeneous activated carbon catalyst. Hungarian Patent Application No. 011706 discloses the oxidation of N-phosphonomethyliminodiacetic acid with peroxide in the presence of metals or metal compounds.

R. J. Motekaitis, A. E. Martell, D. Hayes and W. W. Frenier, Can. J. Chem., 58, 1999 (1980) disclose the iron(III) or copper(II) catalyzed oxidative dealkylation of ethylene diaminetetracetic acid (EDTA) and nitrilotriacetic acid (NTA), both of which have iminodiacetic acid groups. R. J. Motekaitis, X. B. Cox, III, P. Taylor, A. E. Martell, B. Miles and T. J. Tvedt, Can. J. Chem., 60, 1207 (1982) disclose that certain metal ions, such as Ca(II), Mg(II), Fe(II), Zn(II) and Ni(II) chelate with EDTA and stabilize against oxidation, thereby reducing the rate of oxidative dealkylation.

SUMMARY OF THE INVENTION

The present invention involves a process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of a transition metal catalyst.

DETAILED DESCRIPTION OF THE INVENTION

The process of this invention involves contacting N-phosphonomethyliminodiacetic acid with a transition metal catalyst in a mixture or solution. This mixture or solution is contacted with a molecular oxygen-containing gas while heating the reaction mass to a temperature sufficiently elevated to initiate and sustain the oxidation

reaction of N-phosphonomethyliminodiacetic acid to produce N-phosphonomethylglycine.

The transition metal catalyst of the present invention can be any one or more of several transition metal compounds such as manganese, cobalt, iron, nickel, chromium, ruthenium, aluminum, molybdenum, vanadium and cerium. The catalysts can be in the form of salts such as manganese salts, e.g., manganese acetate, manganese sulfate; complexes such as manganese(II)bis(acetylacetonate) (Mn(II)(acac)_2); cobalt salts such as $\text{Co(II)(SO}_4\text{)}$, $\text{Co(II)(acetylacetonate)}$, CoCl_2 , CoBr_2 , $\text{Co(NO}_3\text{)}_2$ and cobalt acetate; cerium salts such as $(\text{NH}_4)_4\text{Ce(SO}_4\text{)}_6$ and $(\text{NH}_4)_2\text{Ce(NO}_3\text{)}_6$, iron salts such as $(\text{NH}_4)_2\text{Fe(SO}_4\text{)}_2$, iron(III) (dicyano) (bisphenanthroline)-2-(tetrafluoroborate) salt and $\text{K}_3\text{Fe(CN)}_6$, and other metal salts such as NiBr_2 , CrCl_3 , $\text{RuCl}_2(\text{Me}_2\text{SO})$, RuBr_3 , $\text{Al(NO}_3\text{)}_3$, $\text{K}_4\text{Mo(CN)}_6$, $\text{VO(acetylacetonate)}_2$ and VOSO_4 . The catalyst can be added to the N-phosphonomethyliminodiacetic acid in the salt form, or a salt may be generated in situ by the addition of a source of a transition metal ion such as MnO_2 which dissolves in the reaction medium. The $\text{Mn(III)chloro(phthalocyaninato)}$, however, is not catalytic, possibly because the phthalocyanine ligand covalently bonds to the Mn(III) and therefore inhibits the formation of N-phosphonomethyliminodiacetic acid/manganese complex in solution.

Manganese salts such as Mn(II), Mn(III) or Mn(IV) salts can be used individually, however, the reaction displays a delayed reaction initiation time (initiation period), e.g., there is a delay before any N-phosphonomethylglycine is produced. When a mixture of Mn(II) and Mn(III) salts are used as a catalyst system, the initiation is diminished or eliminated. A preferred manganese salt catalyst is a mixture of Mn(II) and Mn(III) salts in the range of 1:10 to 10:1 mole ratio of the Mn ions. A most preferred manganese catalyst salt is a 1:1 mole ratio of Mn(II) and Mn(III) ions in the form of manganese acetate salts. A preferred cobalt catalyst is a Co(II) salt such as $\text{Co(II)(SO}_4\text{)}$, Co(II)Cl_2 , Co(II)Br_2 , Co(II)(OH)_2 and Co(II)acetate .

The concentration of the transition metal catalyst in the reaction solution can vary widely, in the range of 0.1 M to 0.0001 M total metal ion concentration. For manganese, the reaction appears to have a first order dependency on the catalyst concentration, e.g., the reaction rate increases linearly as the catalyst concentration increases. The preferred concentration is in the range of about 0.01 M to about 0.001 M, which gives a suitably fast rate of reaction that can be easily controlled and favors selectivity to N-phosphonomethylglycine.

The reaction temperature is sufficient to initiate and sustain the oxidation reaction, in the range of about 25° C. to 150° C. In general, as the reaction temperature increases, the reaction rate increases. To achieve an easily controlled reaction rate and favor selectivity to N-phosphonomethylglycine, a preferred temperature range is about 50° C. to 120° C. and a most preferred is in the range of about 70° C. to 100° C. If a temperature of above about 100° C. is used, pressure will have to be maintained on the system to maintain a liquid phase.

The pressure at which this process is conducted can vary over a wide range. The range can vary from about atmospheric (101 kPa) to about 3000 psig (20700 kPa). A preferred range is about 30 psig (200 kPa) to about 1000 psig (about 6900 kPa). A most preferred range is

from about 150 psig (about 1000 kPa) to 600 psig (about 4140 kPa).

The oxygen concentration, as designated by the partial pressure of oxygen (PO_2), in the reaction affects the reaction rate and the selectivity to the desired product, N-phosphonomethylglycine. As the PO_2 increases, the reaction rate generally increases and the selectivity to N-phosphonomethylglycine increases. The PO_2 can be increased by increasing the overall reaction pressure, or by increasing the molecular oxygen concentration in the molecular oxygen-containing gas. The PO_2 can vary widely, in the range of from 1 psig (6.9 kPa) to 3000 psig (20700 kPa). A preferred range is from 30 psig (207 kPa) to 1000 psig (6900 kPa).

The term "molecular oxygen-containing gas" means molecular oxygen gas or any gaseous mixture containing molecular oxygen with one or more diluents which are non-reactive with the oxygen or with the reactant or product under the conditions of reaction. Examples of such diluent gases are air, helium, argon, nitrogen, or other inert gas, or oxygen-hydrocarbon mixtures. A preferred molecular oxygen is undiluted oxygen gas.

The manner in which the solution or mixture of the N-phosphonomethyliminodiacetic acid is contacted with molecular oxygen can vary greatly. For example, the N-phosphonomethyliminodiacetic acid solution or mixture can be placed in a closed container with some free space containing molecular oxygen and shaken vigorously or agitated by stirring. Alternatively, the molecular oxygen can be continuously bubbled through the solution or mixture containing the transition metal catalyst using a straight tube or a tube with a fritted diffuser attached to it. The process of this invention only requires actively contacting the molecular oxygen containing gas with the aqueous solution or mixture of the N-phosphonomethyliminodiacetic acid containing a transition metal catalyst.

The initial pH (pHi) of the reaction affects the reaction rate and the selectivity to N-phosphonomethylglycine. For example, with manganese, as the initial pH increases, the reaction rate increases, but the selectivity to N-phosphonomethylglycine decreases. The pHi of the reaction can vary widely, in the range of about 0.1 to about 7. A preferred range is about 1 to about 3 with manganese and about 0.1 to 3 with cobalt. A most preferred pH is the unadjusted pH of N-phosphonomethyliminodiacetic acid in a water solution which varies with the N-phosphonomethyliminodiacetic acid concentration and the reaction temperature.

The oxidation reaction can take place in a solution or slurry. For a solution, the initial concentration of the N-phosphonomethyliminodiacetic acid in the reaction mass is a function of the solubility of the N-phosphonomethyliminodiacetic acid in the solvent at both the desired reaction temperature and the pHi of the solution. As the solvent temperature and pH changes, the solubility of the N-phosphonomethyliminodiacetic acid changes. A preferred initial concentration of the N-phosphonomethyliminodiacetic acid is a saturated slurry containing a solvent system at reaction conditions, which maximize the yield of N-phosphonomethylglycine in the reaction mass. A preferred concentration of N-phosphonomethyliminodiacetic acid is in the range of about 1 to 50 wt. %. It is, of course, possible to employ very dilute solutions of N-phosphonomethyliminodiacetic acid, or slurries and mixtures.

The reaction is typically carried out in an aqueous solvent. The term aqueous solvent means solutions con-

taining at least about 50 weight % water. The preferred aqueous solvent is distilled, deionized water.

The following examples are for illustration purposes only and are not intended to limit the scope of the claimed invention.

EXAMPLES

A series of runs were made to oxidize N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine. The reactions were conducted in a modified Fisher-Porter glass pressure apparatus or an Engineer Autoclave 300 ml pressure reactor in which a stirrer was installed in the head, as were three additional valved ports that were used as a sample port, a gas inlet, and a purged gas outlet. The stirrer maintained sufficient agitation to afford thorough gas-liquid mixing. The temperature was controlled by immersing the reactor in a constant temperature oil bath. The indicated amount of transition metal catalyst was dissolved or suspended in a distilled, deionized water solution containing the indicated amount of N-phosphonomethyliminodiacetic acid. The reactor was sealed and heated to the indicated reaction temperature, then pressurized to the indicated PO_2 with oxygen gas. Agitation was initiated.

The selectivity (mole %) to N-phosphonomethylglycine was determined by dividing the moles of N-phosphonomethylglycine produced by the total moles of N-phosphonomethyliminodiacetic acid consumed and multiplying by 100. The yield (mole %) of N-phosphonomethylglycine was determined by dividing the moles of N-phosphonomethylglycine produced by the total moles of starting N-phosphonomethyliminodiacetic acid and multiplying by 100.

EXAMPLES 1 THROUGH 8

Examples 1 through 8, shown in Table 1, show the effect of varying the manganese catalyst concentration. In examples 1-4 the reaction temperature was 90° C., the PO_2 was 100 psig (690 kPa), the initial N-phosphonomethyliminodiacetic acid concentration was 0.1 M. The catalyst was a mixture of Mn(II) and Mn(III) acetate salts in a 1:1 mole ratio of Mn(II) and Mn(III). Examples 5-8 were run at the same conditions as 1-4, except that the PO_2 was 450 psig (3100 kPa) and the reaction temperature was 80° C. and the catalyst was Mn(II) acetate.

TABLE 1

Effect of Varying Catalyst Concentration				
Examp- les	Selectivity to N-phospho- methyl- glycine (Mole %)	Manga- nese Con- centration (M)	Initial Reaction Rate (Velocity, M/hr)	Yield of N-Phospho- methyl glycine (Mole %) at indi- cated time (h)
1	58	0.008	0.23	53(6)
2	82	0.004	0.10	75(6)
3	84	0.002	0.05	18(14)
4	63	0.001	0.016	45(6)
5	83	0.02	0.30	83(1)
6	83	0.0067	0.10	81(1)
7	70	0.004	0.07	68(6)
8	74	0.002	0.034	68(6)

The data indicated that the reaction rate increases with the catalyst concentration. There appeared to be a

first-order dependence of the reaction rate on the catalyst concentration.

EXAMPLES 9 THROUGH 13

Examples 9 through 13, shown in Table 2, illustrate the effect of initial pH on the reaction rate and selectivity to N-phosphonomethylglycine for a manganese catalyst. The reaction temperature was 80° C., the PO₂ was 100 psig (690 kPa), the initial N-phosphonomethyliminodiacetic acid concentration was 0.1 M, the reaction times are indicated and the manganese ion concentration was 0.004 M. The mixture of manganese salts was the same as used in Example 1. The initial pH was adjusted using sodium hydroxide or sulfuric acid solutions. The data indicate that as the initial pH increases, the reaction rate increases, but the selectivity to N-phosphonomethylglycine decreases.

TABLE 2

Effect of Varying Initial pH				
Example	Initial pH	Initial Reaction Rate (M/h)	Yield of N-phosphonomethylglycine (Mole %) at indicated time (h)	Selectivity to N-phosphonomethylglycine (Mole %)(h)
9	1.20	0.0103	31(6)	49(6)
10	1.35	0.015	56(5)	66(5)
11	1.80	0.11	41(24)	44(24)
12	2.30	0.14	36(24)	37(24)
13	3.50	0.32	39(39)	41(4)

EXAMPLES 14 THROUGH 16

Examples 14 through 16, shown in Table 3, illustrate the effect of reaction temperature on reaction rates and selectivity to N-phosphonomethylglycine for a manganese catalyst. The PO₂ was 450 psig, the initial N-phosphonomethyliminodiacetic acid concentration was 0.1 M and the manganese ion concentration was 0.067 M. The form of the manganese salt was Mn(II)SO₄, and the pH was the unadjusted pH of the acid solution.

The data indicated that as the reaction temperature increased, the reaction rate increased.

TABLE 3

Effect of Varying Temperature				
Example	Temperature (°C.)	Initial Reaction Rate (M/hr)	Selectivity to N-phosphonomethylglycine (Mole %) at indicated time (h)	Yield of N-phosphonomethylglycine (Mole %) at indicated time (h)
14	70	0.035	77 (5)	75(5)
15	80	0.093	83 (14)	81(14)
16	90	0.310	80 (4)	77(4)

EXAMPLES 17 THROUGH 22

Examples 17 through 22, shown in Table 4, illustrate the effect of PO₂ on selectivity to N-phosphonomethylglycine for a manganese catalyst. The reaction temperature was 80° C., the initial N-phosphonomethyliminodiacetic acid concentration was 0.1, the reaction time was as indicated which allowed for almost complete conversion for the N-phosphonomethyliminodiacetic acid, and the manganese ion concentration was 0.006 M. The form of the manganese salt was Mn(II)SO₄ and the pH was the unadjusted pH of the acid solution.

The data indicated that as the PO₂ increased, the selectivity to N-phosphonomethylglycine increased.

TABLE 4

Effect of Varying PO ₂			
Example	PO ₂ psig (kPa)	Selectivity to N-phosphonomethylglycine (Mole %) at the indicated time (h)	Yield of N-phosphonomethylglycine (Mole %) at the indicated time (h)
17	40(210)	56(6)	54(6)
18	70(450)	65(6)	63(6)
19	100(690)	68(6)	66(6)
20	130(890)	75(6)	73(6)
21	225(1550)	81(2)	78(2)
22	450(3100)	83(14)	81(14)

EXAMPLES 23 THROUGH 29

AND CONTROL 1

Examples 23 through 29 and Control 1, shown in Table 5, illustrate the effect of varying the form of the manganese catalyst on selectivity to N-phosphonomethylglycine. The reaction temperature was 90° C., the PO₂ was 100 psig (700 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.1 M, the manganese concentration was 0.004 M and the reaction time was 1 h. The pH was the unadjusted pH of the acid solution.

The Mn(III)chloro-(phthalocyanato) (Control 1) was not catalytic.

TABLE 5

Effect of Varying Form of Manganese			
Example	Form	Selectivity to N-phosphonomethylglycine (Mole %) at 1 h.	Selectivity at 6 h.
23	¹ Mn(II)/Mn(III)	43	75
24	Mn(II)acetate	18	75
25	Mn(III)acetate	20	75
26	Mn(II)sulfate	16	75
27	² Mn(II)(acac)	20	75
28	³ MnCl ₂ ·4H ₂ O	82	—
29	⁴ MnO ₂	70	73
Control 1	⁴ Mn(III)	1	<10

¹Mn acetate, 50/50 mole ratio Mn(II)/Mn(III)

²Mn(II)bis(acetylacetonate)

³PO₂ = 450 psig (3100 kPa) at 80° C. and Mn concentration was 0.01M.

⁴Mn(III)chloro-(phthalocyanato)

EXAMPLES 30 THROUGH 42

Examples 30 through 42, shown in Table 6, further illustrate the present invention. The initial pH, unless otherwise indicated, was the unadjusted pH at reaction temperature, the PO₂, unless otherwise indicated, is 100 psig (690 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.1 M, and the manganese catalyst was the mixture used in Example 1.

TABLE 6

Ex-ample	Run Time (h)	Catalyst Concentration (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)
30	1	.01	90	10	96
31	1	.02	80	42	97
32	1 ^a	.007	80	32	91
33	2	.01	70	8	95

TABLE 6-continued

Ex-ample	Run Time (h)	Catalyst Concentration (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)
34	2	.007	80	65	95
35	2 ^b	.007	70	74	96
36	2 ^c	.007	80	25	75
37	2 ^d	.007	80	22	63
38	2	.004	90	42	80
39	2	.002	90	60	75
40 ^e	2½	.007	80	85	100
41 ^f	1	.007	80	95	97
42 ^g	5	.07	80	19	84

^apH = 2.3^bPO₂ = 130 psig (810 kPa)^cPO₂ = 40 psig (275 kPa)^dpH = 1.35^ePO₂ = 225 psig (1545 kPa)^fPO₂ = 450 psig (3100 kPa)^gCatalyst was Mn(II)acetylacetonate, the PO₂ was 450 psi (3000 kPa) and the initial concentration of N-phosphonomethyliminodiacetic acid was 0.5M.

EXAMPLES 43 THROUGH 65

Examples 43 through 65, shown in Table 7, illustrate the use of cobalt catalysts in the present invention. The initial concentration of N-phosphonomethyliminodiacetic acid was 0.1 M and the catalyst was Co(II)(SO₄). The pH was the unadjusted pH of the N-phosphonomethyliminodiacetic acid of the solution, unless otherwise indicated when it was adjusted with sodium hydroxide or sulfuric acid solution.

TABLE 7

Cobalt Catalysts							
Example	Run Time (h)	Catalyst Concentration (M)	Temperature (°C.)	Yield (Mole %)	Conversion (Mole %)	pH	PO ₂ (psi)
43	5.5	0.02	80	73	100	unadjusted	450
44	3.0	0.02	85	85	100	unadjusted	450
45	1.75	0.02	90	75	100	unadjusted	450
46	5.5	0.02	85	90	100	unadjusted	450
47	5	0.02	85	98	100	unadjusted	1000
48	2.0 ^a	0.02	85	21	31	unadjusted	450
49	5.5	0.02	85	74	98	unadjusted	300
50	3.0 ^b	0.036	90	87	100	unadjusted	450
51	4.0 ^c	0.048	80	64	97	unadjusted	450
52	5.0 ^d	0.125	85	52	99	unadjusted	450
53	18 ^e	0.5	100	16	100	6.25	100
54	18 ^e	0.5	100	28	98	1.80	100
55	18 ^e	0.5	100	16	100	2.25	100
56	18 ^e	0.5	100	0	100	4.00	100
57	18 ^e	0.5	100	35	98	1.09	100
58	18 ^e	0.5	100	9.9	22	0.77	100
59	18 ^e	0.5	100	17	98	1.7	100
60	18 ^e	0	100	0	98	9.00	100
61	18 ^e	0.01	100	20	40	0.44	100
62	2 ^f	0.01	100	28	98	1.80	100
63	2 ^g	0.01	100	26	98	1.80	100
64	18 ^h	0.01	100	26	98	1.74	100
65	5 ⁱ	0.2	85	66	99	1.7M	450

^aThe catalyst was Co(III)(acetylacetonate)₃.^bThe initial N-phosphonomethyliminodiacetic acid concentration was 0.3M.^cThe initial N-phosphonomethyliminodiacetic acid concentration was 0.4M.^dThe initial N-phosphonomethyliminodiacetic acid concentration was 1.0M.^eThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5M, the catalyst was CoCl₂.^fThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5M and the catalyst was Co(NO₃)₂.^gThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5M and the catalyst was cobalt acetate.^hThe initial N-phosphonomethyliminodiacetic acid concentration was 0.5M and the catalyst was CoBr₂.ⁱThe initial N-phosphonomethyliminodiacetic acid concentration was 0.4M.

EXAMPLES 66 THROUGH 85

Examples 66 through 85, shown in Table 8, illustrate iron catalysts suitable for the present invention. The PO₂ was 100 psi (690 kPa), the catalyst concentration was 0.01 M, the reaction temperature was 100° C., the run time was 18 h, and the initial concentration of the

N-phosphonomethyliminodiacetic acid was 0.5 M, which formed a slurry. When NaBr was added, the concentration was also 0.01 M.

TABLE 8

Iron Catalysts				
Example	Catalyst	Yield (mole %)	Conversion (mole %)	pH
66	Fe(SO ₄) ₂	21	36	6.25
67	Fe(SO ₄) ₂	18	28	10.0
68	Fe(SO ₄) ₂	6	14	5.0
69	Fe(SO ₄) ₂ + NaBr	5	6	3.0
70	Fe(SO ₄) ₂ + NaBr	12	14	5.0
71	Fe(SO ₄) ₂ + NaBr	26	40	6.25
72	Fe(SO ₄) ₂ + NaBr	28	84	7.0
73	Fe(SO ₄) ₂ + NaBr	29	84	8.0
74	Fe(SO ₄) ₂ + NaBr	37	83	9.0
75	iron(III)(dicyano)bis (o-phenanthroline) tetra-fluoroborate salt	6	12	6.25
76	iron(III)(dicyano)bis (o-phenanthroline) tetra-fluoroborate salt	8	10	7.0
77	iron(III)(dicyano)bis (o-phenanthroline) tetra-fluoroborate salt	3	12	9.0
78	iron(III)(dicyano)bis (o-phenanthroline) tetra-fluoroborate salt	3	12	10.0
79	K ₃ Fe(CN) ₆ ^a	3	14	3.0
80	K ₃ Fe(CN) ₆ ^a	8	24	5.0
81	K ₃ Fe(CN) ₆ ^a	21	46	6.3
82	K ₃ Fe(CN) ₆ ^a	30	76	7.0
83	K ₃ Fe(CN) ₆ ^a	37	80	9.0
84	K ₃ Fe(CN) ₆ ^a	32	80	10.0

85 Fe(SO₄)₂ + Al(NO₃)₃ 21 72 6.0^aRun time is 8 h.

EXAMPLES 86 THROUGH 106 AND CONTROL 2

Examples 86 through 106 and Control 2, shown in Table 9, illustrate nickel, chromium, ruthenium, aluminum, and molybdenum catalysts appropriate for the present invention. The conditions are as for those given in Table 8. The catalyst for Control 2, CuCl_2 , appeared to be ineffective.

TABLE 9

Nickel Chromium, Ruthenium, Aluminum and Molybdenum Catalysts		Yield (mole %)	Conversion (mole %)	pH
Examples	Catalyst			
86	NiBr_2	0.2	22	5.0
87	NiBr_2	0.2	10	4.0
88	NiBr_2	10	34	7.0
89	NiBr_2	9	38	8.4
90	NiBr_2	8	34	10.4
91	CrCl_3	1	12	1.26
92	CrCl_3	4	16	2.0
93	CrCl_3	16	76	3.0
94	CrCl_3	0.1	14	4.0
95	CrCl_3	12	52	5.0
96	CrCl_3	4	22	7.0
97	CrCl_3	13	58	6.25
98	RuBr_3	70	8	6.25
99	RuBr_3	18	34	10.0
100	$\text{RuBr}_2(\text{Me}_2\text{SO})_4$	34	62	6.25
101	$\text{RuBr}_2(\text{Me}_2\text{SO})_4$	25	48	11.0
102	$\text{Al}(\text{NO}_3)_3$	11	34	6.25
103	$\text{Al}(\text{NO}_3)_3 + \text{NaCl}$	12	16	6.25
Control 2	CuCl_2	0.2	14	6.25
104	$\text{K}_4\text{Mo}(\text{CN})_8$	4	22	4.0
105	$\text{K}_4\text{Mo}(\text{CN})_8$	32	48	6.0
106	$\text{K}_4\text{Mo}(\text{CN})_8$	10	30	9.0

EXAMPLES 107-109

Examples 107 through 109 shown in Table 10, illustrate vanadium catalysts suitable for the present invention. The reaction temperature was 70° C., the PO_2 was 100 psi (690 kPa), the initial concentration of N-phosphonomethyliminodiacetic acid was 0.5 M, the catalyst concentration was 0.033 M.

TABLE 10

Vanadium Catalysts		Run Time (h)	Yield (mole %)	Conversion (mole %)
Examples	Catalyst			
107	$\text{VO}(\text{acetylacetonate})_2$	2	40	67
108	$\text{VO}_2(\text{hydrate})$	2.25	42	94
109	$\text{VO}_2(\text{hydrate})^a$	5	54	91

^aThe initial concentration of N-phosphonomethyliminodiacetic acid was 0.15M and the concentration of catalyst was 0.015M.

EXAMPLES 110 AND 111

Examples 110 and 111 shown in Table 11 illustrate cerium catalysts suitable for the present invention. The reaction temperature was 90° C. and the PO_2 was 130 psi (897 kPa).

TABLE 11

Cerium Catalysts		N-phosphonomethyliminodiacetic acid			
Example	Catalyst	Run Time (h)	Catalyst Concentration (M)	Concentration (M)	Yield (mole %)
110	$\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4$	3	0.1	1.0	7
111	$\text{Ce}(\text{NH}_4)_4(\text{SO}_4)_4$	3	0.01	0.1	30

We claim:

1. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of iron, nickel, chromium, ruthenium, aluminum, molybdenum, vanadium and cerium.

2. The process of claim 1 wherein the catalyst is at least one of an iron(III), a nickel(II), a chromium(III), a ruthenium(II), a ruthenium(III), an aluminum(III), a molybdenum(IV), a molybdenum(V), a molybdenum(VI), a vanadium(IV), a vanadium(V), a cerium(III) and a cerium(IV) salt.

3. The process of claim 1 wherein the catalyst is selected from the group consisting of iron(III) diammonium disulfate, vanadiumoxy (acetylacetonate), and vanadiumoxysulfate (hydrate).

4. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with molecular oxygen in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of vanadium and cerium, wherein the reaction temperature is in the range of about 25° C. to 150° C., the reaction pressure is in the range of about atmospheric (101 kPa) to about 3000 psig (20,700 kPa), the partial pressure of oxygen is in the range of about 1 psig (6.9 kPa) to about 3000 psig (20,700 kPa) and the initial pH is in the range of about 0.1 to 7.0.

5. The process of claim 1 wherein the catalyst is at least one of a vanadium(IV), a vanadium(V), a cerium(III) and a cerium(IV) salt.

6. The process of claim 1 wherein the N-phosphonomethyliminodiacetic acid is present as a slurry.

7. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of iron, nickel and ruthenium.

8. The process of claim 7 wherein the catalyst is at least one of an iron(III), a nickel(II), a ruthenium(II), or a ruthenium(III) salt.

9. The process of claim 7 wherein the catalyst is iron(III) diammonium disulfate.

10. A process for the production of N-phosphonomethylglycine comprising contacting N-phosphonomethyliminodiacetic acid with a molecular oxygen-containing gas in the presence of an aqueous soluble catalyst selected from the group consisting of the salts and salt complexes of iron and nickel.

11. The process of claim 10 wherein the catalyst is at least one of an iron(III) or a nickel(II) salt.

12. The process of claim 10 wherein the catalyst is iron(III) diammonium disulfate.

13. The process of claim 7 or 10 wherein the N-phosphonomethyliminodiacetic acid is present as a slurry.

14. A process for the production of N-phosphonome-
thylglycine comprising contacting N-phosphonome-
thyliminodiacetic acid with a molecular oxygen-con-
taining gas in the presence of an aqueous soluble cata-

lyst selected from the group consisting of the salts and
salt complexes of nickel.

15. The process of claim 14 wherein the catalyst is a
nickel(II) salt.

16. The process of claim 14 wherein the N-phos-
phonomethyliminodiacetic acid is present as a slurry.

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United States Patent [19]
Fields, Jr.

[11] **Patent Number:** 5,077,430
[45] **Date of Patent:** Dec. 31, 1991

[54] **PEROXIDE PROCESS FOR PRODUCING
N-PHOSPHONOMETHYLGLYCINE**

[75] **Inventor:** Donald L. Fields, Jr., Manchester,
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[73] **Assignee:** Monsanto Company, St. Louis, Mo.

[21] **Appl. No.:** 684,751

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[51] **Int. Cl.:** C07F 9/38

[52] **U.S. Cl.:** 562/17

[58] **Field of Search** 562/17

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[57] **ABSTRACT**

A process is provided for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid with a peroxide to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide. Thereafter, the N-phosphonomethyliminodiacetic acid-N-oxide is converted to N-phosphonomethylglycine by adding a catalytic amount of a metal selected from the group consisting of iron, zinc, aluminum, vanadium and copper, or a compound selected from the group consisting of water-soluble vanadium compounds, ferrous salts and cuprous salts.

3 Claims, No Drawings

PEROXIDE PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a division of application Ser. No. 07/542,995 filed June 25, 1990.

BACKGROUND OF THE INVENTION

This invention relates to a process for the preparation of N-phosphonomethylglycine, and more particularly to the preparation of N-phosphonomethylglycine by the conversion of N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine using peroxides.

N-Phosphonomethylglycine, known also by its common name glyphosate, is a highly effective, commercially important, phytotoxicant useful in controlling a large variety of weeds. It is applied to the foliage of a very broad spectrum of annual and perennial grasses and broadleaf plants. Industrial uses include control of weeds along roadsides, waterways, transmission lines, in storage areas, and in other nonagricultural areas. Usually, N-phosphonomethylglycine is formulated into herbicidal compositions in the form of its various salts in solution, preferably water.

U.S. Pat. No. 3,950,402 to Franz discloses a process for the production of N-phosphonomethylglycine by forming an admixture of N-phosphonomethyliminodiacetic acid, water, and a metallic catalyst selected from the noble metals, heating the admixture to an elevated temperature (greater than 70° C. to avoid low yields) and contacting the admixture with a free oxygen-containing gas.

U.S. Pat. No. 3,954,848 to Franz discloses a process for the production of N-phosphonomethylglycine by reacting N-phosphonomethyliminodiacetic acid with an oxidizing agent, such as hydrogen peroxide, in an aqueous acidic medium in the presence of a strong acid at a temperature of from about 70° C. to about 100° C. It is disclosed that one should employ at least 2 moles of the hydrogen peroxide for each mole of the N-phosphonomethyliminodiacetic acid, and preferably more.

Hungarian Patent Application No. 187,347 discloses a process for the preparation of N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid with peroxides using a catalytic amount of a metal compound selected from compounds of silver, iron, tin, lead, manganese or molybdenum. Molybdates are preferred. At temperatures lower than 80° C., usually a contaminated end product is obtained. Typically, the reaction is carried out at a temperature of above 80° C. and preferably above 100° C. at pressures exceeding atmospheric, wherein the intermediate N-oxide is decomposed as rapidly as it forms. It is further disclosed that two mole equivalents of peroxide should be used for each mole of N-phosphonomethyliminodiacetic acid to obtain acceptable yields of N-phosphonomethylglycine.

Although satisfactory results are obtained by the above processes to make N-phosphonomethylglycine, all of them suffer from one or more disadvantages, such as the use of excessive amounts of peroxide, the use of strong mineral acids and/or reaction at elevated temperatures and pressures. Now, there is provided a process which produces N-phosphonomethylglycine in high yields at modest temperatures and at atmospheric pressure using substantially stoichiometric amounts of

peroxide to oxidize the N-phosphonomethyliminodiacetic acid to the desired N-phosphonomethylglycine without using strong mineral acids, such as hydrochloric acid or sulfuric acid.

SUMMARY OF THE INVENTION

These and other advantages are achieved in a process for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid with peroxide to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide, the improvement which comprises adding a catalytic amount of a metal selected from the group consisting of iron, zinc, aluminum, vanadium and copper, or a compound selected from the group consisting of water-soluble vanadium salts, ferrous salts, and cuprous salts.

DETAILED DESCRIPTION OF THE INVENTION

The intermediate, N-phosphonomethyliminodiacetic acid-N-oxide, is known to those skilled in the art, and can be prepared by a number of methods. For example, the intermediate can be prepared by the teachings in U.S. Pat. No. 3,950,402 or U.S. Pat. No. 3,954,848, both to Franz. In Hungarian Patent Application 187,347, the intermediate is formed from N-phosphonomethyliminodiacetic acid using peroxides in the presence of compounds of silver, iron, tin, lead, manganese or molybdenum. In U.S. Pat. No. 4,062,669 to Franz, an N-organo-N-phosphonomethylglycine is oxidized with peroxide under acidic or basic conditions. Other methods may be known to those skilled in the art.

Any number of peroxides known to those skilled in the art can be used to prepare the N-phosphonomethyliminodiacetic acid-N-oxide. Suitable peroxides include hydrogen peroxide, performic acid, peracetic acid, perbenzoic acid, peroxytrifluoroacetic acid, benzoyl peroxide, benzenepersulfonic acid, and the like. Hydrogen peroxide is preferred, and it is advantageous to use hydrogen peroxide in the form of a concentrated solution, say between about 30% and 60%.

In the process of the present invention, it is preferred to prepare the N-phosphonomethyliminodiacetic acid-N-oxide by contacting N-phosphonomethyliminodiacetic acid with a peroxide in the presence of a catalytic amount of a water-soluble molybdenum compound or a water-soluble tungsten compound. A water-soluble tungsten compound is especially preferred.

The temperature of the process to prepare the N-phosphonomethyliminodiacetic acid-N-oxide can vary from as low as about 20° C. to about 70° C. Although temperatures below about 20° C. can be used, such temperatures would require the use of cooling, and no advantages are obtained. At temperatures above about 70° C., degradation of the N-phosphonomethyliminodiacetic acid-N-oxide is observed, which affects the final yield of the desired N-phosphonomethylglycine. Temperatures between about 20° C. and about 65° C. are preferred.

The salts of tungsten useful as catalysts to oxidize the N-phosphonomethyliminodiacetic acid to the N-phosphonomethyliminodiacetic acid-N-oxide are known to those skilled in the art. It is only necessary that the tungsten salts are soluble in the reaction medium. Suitable tungsten compounds include tungstic acid, 1,2-tungstophosphate, and barium tungstate. The alkali metal tungstates, such as sodium tungstate, potassium

tungstate, and the like, provide satisfactory results, and the alkali metal tungstates are preferred.

The salts of molybdenum useful as catalysts to oxidize the N-phosphonomethyliminodiacetic acid to the N-phosphonomethyliminodiacetic acid-N-oxide are also known to those skilled in the art. It is only necessary that the molybdenum salts are soluble in the reaction medium. Suitable molybdenum compounds include molybdenum halides, such as molybdenyl trichloride and the like, alkali metal molybdates, such as sodium molybdate and the like, or more complex salts, such as the ammonium or alkali metal dimolybdates. Sodium and ammonium molybdates are preferred.

The amount of catalyst to convert the N-phosphonomethyliminodiacetic acid to the intermediate N-phosphonomethyliminodiacetic acid-N-oxide can vary within wide limits. Concentrations between about 0.01 and about 5 wt. % catalyst, based on the weight of the N-phosphonomethyliminodiacetic acid, provide satisfactory results. At concentrations of less than about 0.01 wt. % catalyst, the reaction is slow, and at concentrations greater than about 5 wt. %, no particular advantage is seen, although such higher concentrations are not harmful. It is preferred to use between about 0.01 wt. % and about 1 wt. % based on the weight of the N-phosphonomethyliminodiacetic acid.

In the process of the present invention, the amount of peroxide should be the stoichiometric amount required to convert the N-phosphonomethyliminodiacetic acid to the intermediate N-phosphonomethyliminodiacetic acid-N-oxide. As will occur to those skilled in the art, when less than the stoichiometric amount of peroxide is used, the yield of the desired N-phosphonomethylglycine is lower. A slight excess of peroxide can be used to insure a quantitative conversion of the N-phosphonomethyliminodiacetic acid to the intermediate, but there is no advantage to using large excesses of peroxide, and excesses of peroxide may be deleterious if water-soluble compounds, such as ferrous salts or cuprous salts, are used to convert the intermediate to N-phosphonomethylglycine.

Regardless of the method used to prepare the N-phosphonomethyliminodiacetic acid-N-oxide from the N-phosphonomethyliminodiacetic acid, the intermediate is contacted with a catalytic amount of a substance selected from the group consisting of iron metal, zinc metal, aluminum metal, vanadium metal or copper metal. Alternatively, a compound selected from the group consist of the water-soluble salts of a vanadium compound, ferrous salts, and cuprous salts can convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to the desired N-phosphonomethylglycine. Suitable vanadium compounds that are soluble in the reaction mixture include vanadium pentoxide, vanadium sulfate, vanadium chloride and the like. Suitable water-soluble ferrous compounds that can be used in the process of the present invention include ferrous sulfate, ferrous halides, such as ferrous chloride, ferrous bromide and the like. Suitable water-soluble cuprous salts that can be used in the process of the present invention include cuprous chloride, cuprous bromide, cuprous sulfate and the like. Of the water-soluble compounds, vanadium compounds are preferred, and vanadyl sulfate is especially preferred.

The amount of catalyst to convert the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine depends upon the catalyst used and the amount of peroxide in excess of that required to

produce the intermediate from the N-phosphonomethyliminodiacetic acid. When metals such as iron, zinc, aluminum, vanadium and copper are used, the rate of reaction to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine depends upon the surface area of the metal present, and it is preferred to use from about 0.1 wt. % to about 10 wt. % of the metal, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide present. In addition, it is preferred to use the metal in any form that provides a high surface area, for example, a wool, a powder or finely divided granules. However, when a water-soluble compound is used as a catalyst, the excess peroxide will react with the water-soluble compound, and in addition to the amount of compound required to react with the excess peroxide, there should also be a sufficient amount of the water-soluble compound to catalyze the reaction of the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine. The amount of water-soluble compound remaining after reaction with the peroxide to act as a catalyst should be at least 0.005 wt. %, based on the amount of the N-phosphonomethyliminodiacetic acid-N-oxide. Excess water-soluble compound as high as 5%, or even higher, can be used, but there does not seem to be an advantage to using such higher concentrations for the conversion of the intermediate to N-phosphonomethylglycine, although such higher concentrations are not harmful. It is preferred to use between about 0.01 wt. % and about 2 wt. % of the water-soluble compound, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide, after reaction with any excess peroxides.

The temperature required to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to the desired N-phosphonomethylglycine can vary within wide limits. It is preferred to add the catalyst at or near room temperature (about 20° C.) because vigorous gas evolution frequently occurs, and the conversion of N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine is exothermic. It is preferred to keep the reaction temperature below about 80° C. by cooling the reaction vessel or using a low catalyst charge. Temperatures above about 80° C. will provide N-phosphonomethylglycine, but some yield loss may occur.

The concentration of the N-phosphonomethyliminodiacetic acid as the starting material can vary within wide limits in the process of the present invention. For example, an aqueous suspension containing up to 50 wt. % N-phosphonomethyliminodiacetic acid can be used. Higher concentrations of the N-phosphonomethyliminodiacetic acid can be used, but it can present processing difficulties because of the thickness of the slurry. On the other hand, an aqueous solution of the N-phosphonomethyliminodiacetic acid containing about 5 wt. % of the N-phosphonomethyliminodiacetic acid can also be used. Lower concentrations can also be used, but it requires processing large volumes of liquid in the process of the present invention. It is preferred to use an aqueous slurry containing from about 20 wt. % to about 40 wt. % of the N-phosphonomethyliminodiacetic acid.

The N-phosphonomethyliminodiacetic acid starting material can be prepared by methods known to those skilled in the art. For example, this material can be produced by the reaction of formaldehyde, iminodiacetic acid and orthophosphorous acid in the presence of

sulfuric acid. Although the N-phosphonomethyliminodiacetic acid mixture resulting from this reaction can be employed directly in the process of this invention, it is preferred to isolate the N-phosphonomethyliminodiacetic acid and then employ it herein.

This invention is further illustrated by, but not limited to, the following examples. Conversion is calculated by dividing the moles of other compounds produced by the moles of starting N-phosphonomethyliminodiacetic acid and multiplying by 100. Selectivity is calculated by dividing the moles of N-phosphonomethylglycine produced by the moles of N-phosphonomethyliminodiacetic acid converted and multiplying by 100.

EXAMPLE 1

This Example illustrates the process of the present invention using a water-soluble vanadium salt to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

(A) To a 100 ml round bottomed flask was added water (25 ml), N-phosphonomethyliminodiacetic acid (20 g), 47% hydrogen peroxide (7.1 g) and sodium tungstate (0.05 g). The mixture was heated to 65° C. and maintained at this temperature until a solution was obtained (about 58 minutes), indicating the N-oxide was formed. The solution was then allowed to cool to about 55° C. and stirred for an additional 30 minutes.

(B) After cooling to room temperature, vanadyl sulfate (0.05 g, 29% water content) was added to the solution. After stirring for about 5 minutes, the color of the solution changed from blue to light green. Gas evolution began with a slow exotherm. When the temperature reached about 40° C., the exotherm greatly accelerated to 65° C. and cooling water was applied to maintain the solution at this temperature. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrate and solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 96.7%, and the selectivity to N-phosphonomethylglycine was 91.4%.

EXAMPLE 2

This Example illustrates the process of the present invention using a water-soluble ferrous salt to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

The procedure of Example 1 Step (A) was repeated. Then after the solution was allowed to cool to room temperature, ferrous sulfate (0.02 g) was added to the solution. Gas evolution was observed, and the temperature of the solution rose to 65° C. Cooling water was applied to keep the temperature below 70° C. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrate and solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 99.5%, and the selectivity to N-phosphonomethylglycine was 93.7%.

EXAMPLE 3

This Example illustrates the process of the present invention using zinc metal to convert N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

thyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

(A) To a 100 ml round bottomed glass flask was added water (37 ml), N-phosphonomethyliminodiacetic acid (14.0 g), 30% hydrogen peroxide (7.2 g) and ammonium dimolybdate tetrahydrate (0.32 g). The mixture was heated to 65° C. and maintained at this temperature until a solution was obtained (about 30 minutes), indicating the N-oxide was formed. The solution was then allowed to cool to 45° C. and stirred for 50 minutes.

(B) After cooling to room temperature, zinc metal powder (0.4 g) was added to the solution. Vigorous gas evolution was observed, and the temperature of the solution rose to 55° C. in about a 10-minute period. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrate and solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 91.0%, and the selectivity to N-phosphonomethylglycine was 93.8%.

EXAMPLE 4

This Example illustrates the use of copper metal, aluminum metal, and a water-soluble cuprous salt to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

The procedure of Example 3 Step (A) was repeated. After cooling to room temperature, small aliquots of the solution containing the N-phosphonomethyliminodiacetic acid-N-oxide were taken and placed in 25 ml beakers. To one aliquot was added a copper penny. To another aliquot was added aluminum foil. To a third aliquot was added a small amount of cuprous chloride, and to a fourth aliquot was added vanadium metal. In all cases, gas evolution was observed, indicating that the intermediate N-phosphonomethyliminodiacetic acid-N-oxide was converted to N-phosphonomethylglycine.

Although the invention has been described in terms of specified embodiments which are set forth in considerable detail, it should be understood that this is by way of illustration only, and that alternative embodiments and operating techniques will become apparent to those skilled in the art in view of the disclosure. Accordingly, modifications can be made without departing from the spirit of the described invention.

What is claimed is:

1. A process for producing N-phosphonomethylglycine which comprises oxidizing N-phosphonomethyliminodiacetic acid with a peroxide to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide, and then adding a catalytic amount of a ferrous salt to convert the intermediate to N-phosphonomethylglycine.

2. A process of claim 1 wherein the amount of catalyst to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine is between about 0.005 wt% and about 5 wt. %, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide present.

3. A process of claim 2 wherein the amount of catalyst is between about 0.01 wt. % and about 2.0 wt. %.

* * * * *

United States Patent [19]
Fields, Jr.

[11] **Patent Number:** **5,077,430**
[45] **Date of Patent:** **Dec. 31, 1991**

[54] **PEROXIDE PROCESS FOR PRODUCING
N-PHOSPHONOMETHYLGLYCINE**

4,952,723 8/1990 Fields et al. 562/17
5,023,369 6/1991 Fields 562/17

[75] **Inventor:** Donald L. Fields, Jr., Manchester,
Mo.

FOREIGN PATENT DOCUMENTS

0187347 7/1981 Hungary .

[73] **Assignee:** Monsanto Company, St. Louis, Mo.

Primary Examiner—Bruce Gray
Attorney, Agent, or Firm—Frank D. Shearin

[21] **Appl. No.:** 684,751

[22] **Filed:** Apr. 15, 1991

[57] **ABSTRACT**

Related U.S. Application Data

[62] Division of Ser. No. 542,995, Jun. 25, 1990.

[51] **Int. Cl.** C07F 9/38

[52] **U.S. Cl.** 562/17

[58] **Field of Search** 562/17

[56] **References Cited**

U.S. PATENT DOCUMENTS

3,950,402 4/1976 Franz 260/502.5
3,954,848 5/1976 Franz 260/502.5
4,853,159 8/1989 Riley et al. 562/17
4,898,972 2/1990 Fields et al. 562/17

A process is provided for producing N-phosphonome-
thylglycine by the oxidation of N-phosphonome-
thyliminodiacetic acid with a peroxide to form an inter-
mediate N-phosphonomethyliminodiacetic acid-N-
oxide. Thereafter, the N-phosphonomethyliminodia-
cetic acid-N-oxide is converted to N-phosphonome-
thylglycine by adding a catalytic amount of a metal
selected from the group consisting of iron, zinc, alumi-
num, vanadium and copper, or a compound selected
from the group consisting of water-soluble vanadium
compounds, ferrous salts and cuprous salts.

3 Claims, No Drawings

PEROXIDE PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a division of application Ser. No. 07/542,995 filed June 25, 1990.

BACKGROUND OF THE INVENTION

This invention relates to a process for the preparation of N-phosphonomethylglycine, and more particularly to the preparation of N-phosphonomethylglycine by the conversion of N-phosphonomethyliminodiacetic acid to N-phosphonomethylglycine using peroxides.

N-Phosphonomethylglycine, known also by its common name glyphosate, is a highly effective, commercially important, phytotoxicant useful in controlling a large variety of weeds. It is applied to the foliage of a very broad spectrum of annual and perennial grasses and broadleaf plants. Industrial uses include control of weeds along roadsides, waterways, transmission lines, in storage areas, and in other nonagricultural areas. Usually, N-phosphonomethylglycine is formulated into herbicidal compositions in the form of its various salts in solution, preferably water.

U.S. Pat. No. 3,950,402 to Franz discloses a process for the production of N-phosphonomethylglycine by forming an admixture of N-phosphonomethyliminodiacetic acid, water, and a metallic catalyst selected from the noble metals, heating the admixture to an elevated temperature (greater than 70° C. to avoid low yields) and contacting the admixture with a free oxygen-containing gas.

U.S. Pat. No. 3,954,848 to Franz discloses a process for the production of N-phosphonomethylglycine by reacting N-phosphonomethyliminodiacetic acid with an oxidizing agent, such as hydrogen peroxide, in an aqueous acidic medium in the presence of a strong acid at a temperature of from about 70° C. to about 100° C. It is disclosed that one should employ at least 2 moles of the hydrogen peroxide for each mole of the N-phosphonomethyliminodiacetic acid, and preferably more.

Hungarian Patent Application No. 187,347 discloses a process for the preparation of N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid with peroxides using a catalytic amount of a metal compound selected from compounds of silver, iron, tin, lead, manganese or molybdenum. Molybdates are preferred. At temperatures lower than 80° C., usually a contaminated end product is obtained. Typically, the reaction is carried out at a temperature of above 80° C. and preferably above 100° C. at pressures exceeding atmospheric, wherein the intermediate N-oxide is decomposed as rapidly as it forms. It is further disclosed that two mole equivalents of peroxide should be used for each mole of N-phosphonomethyliminodiacetic acid to obtain acceptable yields of N-phosphonomethylglycine.

Although satisfactory results are obtained by the above processes to make N-phosphonomethylglycine, all of them suffer from one or more disadvantages, such as the use of excessive amounts of peroxide, the use of strong mineral acids and/or reaction at elevated temperatures and pressures. Now, there is provided a process which produces N-phosphonomethylglycine in high yields at modest temperatures and at atmospheric pressure using substantially stoichiometric amounts of

peroxide to oxidize the N-phosphonomethyliminodiacetic acid to the desired N-phosphonomethylglycine without using strong mineral acids, such as hydrochloric acid or sulfuric acid.

SUMMARY OF THE INVENTION

These and other advantages are achieved in a process for producing N-phosphonomethylglycine by the oxidation of N-phosphonomethyliminodiacetic acid with peroxide to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide, the improvement which comprises adding a catalytic amount of a metal selected from the group consisting of iron, zinc, aluminum, vanadium and copper, or a compound selected from the group consisting of water-soluble vanadium salts, ferrous salts, and cuprous salts.

DETAILED DESCRIPTION OF THE INVENTION

The intermediate, N-phosphonomethyliminodiacetic acid-N-oxide, is known to those skilled in the art, and can be prepared by a number of methods. For example, the intermediate can be prepared by the teachings in U.S. Pat. No. 3,950,402 or U.S. Pat. No. 3,954,848, both to Franz. In Hungarian Patent Application 187,347, the intermediate is formed from N-phosphonomethyliminodiacetic acid using peroxides in the presence of compounds of silver, iron, tin, lead, manganese or molybdenum. In U.S. Pat. No. 4,062,669 to Franz, an N-organo-N-phosphonomethylglycine is oxidized with peroxide under acidic or basic conditions. Other methods may be known to those skilled in the art.

Any number of peroxides known to those skilled in the art can be used to prepare the N-phosphonomethyliminodiacetic acid-N-oxide. Suitable peroxides include hydrogen peroxide, performic acid, peracetic acid, perbenzoic acid, peroxytrifluoroacetic acid, benzoyl peroxide, benzenepersulfonic acid, and the like. Hydrogen peroxide is preferred, and it is advantageous to use hydrogen peroxide in the form of a concentrated solution, say between about 30% and 60%.

In the process of the present invention, it is preferred to prepare the N-phosphonomethyliminodiacetic acid-N-oxide by contacting N-phosphonomethyliminodiacetic acid with a peroxide in the presence of a catalytic amount of a water-soluble molybdenum compound or a water-soluble tungsten compound. A water-soluble tungsten compound is especially preferred.

The temperature of the process to prepare the N-phosphonomethyliminodiacetic acid-N-oxide can vary from as low as about 20° C. to about 70° C. Although temperatures below about 20° C. can be used, such temperatures would require the use of cooling, and no advantages are obtained. At temperatures above about 70° C., degradation of the N-phosphonomethyliminodiacetic acid-N-oxide is observed, which affects the final yield of the desired N-phosphonomethylglycine. Temperatures between about 20° C. and about 65° C. are preferred.

The salts of tungsten useful as catalysts to oxidize the N-phosphonomethyliminodiacetic acid to the N-phosphonomethyliminodiacetic acid-N-oxide are known to those skilled in the art. It is only necessary that the tungsten salts are soluble in the reaction medium. Suitable tungsten compounds include tungstic acid, 1,2-tungstophosphate, and barium tungstate. The alkali metal tungstates, such as sodium tungstate, potassium

tungstate, and the like, provide satisfactory results, and the alkali metal tungstates are preferred.

The salts of molybdenum useful as catalysts to oxidize the N-phosphonomethyliminodiacetic acid to the N-phosphonomethyliminodiacetic acid-N-oxide are also known to those skilled in the art. It is only necessary that the molybdenum salts are soluble in the reaction medium. Suitable molybdenum compounds include molybdenum halides, such as molybdenyl trichloride and the like, alkali metal molybdates, such as sodium molybdate and the like, or more complex salts, such as the ammonium or alkali metal dimolybdates. Sodium and ammonium molybdates are preferred.

The amount of catalyst to convert the N-phosphonomethyliminodiacetic acid to the intermediate N-phosphonomethyliminodiacetic acid-N-oxide can vary within wide limits. Concentrations between about 0.01 and about 5 wt. % catalyst, based on the weight of the N-phosphonomethyliminodiacetic acid, provide satisfactory results. At concentrations of less than about 0.01 wt. % catalyst, the reaction is slow, and at concentrations greater than about 5 wt. %, no particular advantage is seen, although such higher concentrations are not harmful. It is preferred to use between about 0.01 wt. % and about 1 wt. % based on the weight of the N-phosphonomethyliminodiacetic acid.

In the process of the present invention, the amount of peroxide should be the stoichiometric amount required to convert the N-phosphonomethyliminodiacetic acid to the intermediate N-phosphonomethyliminodiacetic acid-N-oxide. As will occur to those skilled in the art, when less than the stoichiometric amount of peroxide is used, the yield of the desired N-phosphonomethylglycine is lower. A slight excess of peroxide can be used to insure a quantitative conversion of the N-phosphonomethyliminodiacetic acid to the intermediate, but there is no advantage to using large excesses of peroxide, and excesses of peroxide may be deleterious if water-soluble compounds, such as ferrous salts or cuprous salts, are used to convert the intermediate to N-phosphonomethylglycine.

Regardless of the method used to prepare the N-phosphonomethyliminodiacetic acid-N-oxide from the N-phosphonomethyliminodiacetic acid, the intermediate is contacted with a catalytic amount of a substance selected from the group consisting of iron metal, zinc metal, aluminum metal, vanadium metal or copper metal. Alternatively, a compound selected from the group consist of the water-soluble salts of a vanadium compound, ferrous salts, and cuprous salts can convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to the desired N-phosphonomethylglycine. Suitable vanadium compounds that are soluble in the reaction mixture include vanadium pentoxide, vanadium sulfate, vanadium chloride and the like. Suitable water-soluble ferrous compounds that can be used in the process of the present invention include ferrous sulfate, ferrous halides, such as ferrous chloride, ferrous bromide and the like. Suitable water-soluble cuprous salts that can be used in the process of the present invention include cuprous chloride, cuprous bromide, cuprous sulfate and the like. Of the water-soluble compounds, vanadium compounds are preferred, and vanadyl sulfate is especially preferred.

The amount of catalyst to convert the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine depends upon the catalyst used and the amount of peroxide in excess of that required to

produce the intermediate from the N-phosphonomethyliminodiacetic acid. When metals such as iron, zinc, aluminum, vanadium and copper are used, the rate of reaction to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine depends upon the surface area of the metal present, and it is preferred to use from about 0.1 wt. % to about 10 wt. % of the metal, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide present. In addition, it is preferred to use the metal in any form that provides a high surface area, for example, a wool, a powder or finely divided granules. However, when a water-soluble compound is used as a catalyst, the excess peroxide will react with the water-soluble compound, and in addition to the amount of compound required to react with the excess peroxide, there should also be a sufficient amount of the water-soluble compound to catalyze the reaction of the N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine. The amount of water-soluble compound remaining after reaction with the peroxide to act as a catalyst should be at least 0.005 wt. %, based on the amount of the N-phosphonomethyliminodiacetic acid-N-oxide. Excess water-soluble compound as high as 5%, or even higher, can be used, but there does not seem to be an advantage to using such higher concentrations for the conversion of the intermediate to N-phosphonomethylglycine, although such higher concentrations are not harmful. It is preferred to use between about 0.01 wt. % and about 2 wt. % of the water-soluble compound, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide, after reaction with any excess peroxides.

The temperature required to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to the desired N-phosphonomethylglycine can vary within wide limits. It is preferred to add the catalyst at or near room temperature (about 20° C.) because vigorous gas evolution frequently occurs, and the conversion of N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine is exothermic. It is preferred to keep the reaction temperature below about 80° C. by cooling the reaction vessel or using a low catalyst charge. Temperatures above about 80° C. will provide N-phosphonomethylglycine, but some yield loss may occur.

The concentration of the N-phosphonomethyliminodiacetic acid as the starting material can vary within wide limits in the process of the present invention. For example, an aqueous suspension containing up to 50 wt. % N-phosphonomethyliminodiacetic acid can be used. Higher concentrations of the N-phosphonomethyliminodiacetic acid can be used, but it can present processing difficulties because of the thickness of the slurry. On the other hand, an aqueous solution of the N-phosphonomethyliminodiacetic acid containing about 5 wt. % of the N-phosphonomethyliminodiacetic acid can also be used. Lower concentrations can also be used, but it requires processing large volumes of liquid in the process of the present invention. It is preferred to use an aqueous slurry containing from about 20 wt. % to about 40 wt. % of the N-phosphonomethyliminodiacetic acid.

The N-phosphonomethyliminodiacetic acid starting material can be prepared by methods known to those skilled in the art. For example, this material can be produced by the reaction of formaldehyde, iminodiacetic acid and orthophosphorous acid in the presence of

sulfuric acid. Although the N-phosphonomethyliminodiacetic acid mixture resulting from this reaction can be employed directly in the process of this invention, it is preferred to isolate the N-phosphonomethyliminodiacetic acid and then employ it herein.

This invention is further illustrated by, but not limited to, the following examples. Conversion is calculated by dividing the moles of other compounds produced by the moles of starting N-phosphonomethyliminodiacetic acid and multiplying by 100. Selectivity is calculated by dividing the moles of N-phosphonomethylglycine produced by the moles of N-phosphonomethyliminodiacetic acid converted and multiplying by 100.

EXAMPLE 1

This Example illustrates the process of the present invention using a water-soluble vanadium salt to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

(A) To a 100 ml round bottomed flask was added water (25 ml), N-phosphonomethyliminodiacetic acid (20 g), 47% hydrogen peroxide (7.1 g) and sodium tungstate (0.05 g). The mixture was heated to 65° C. and maintained at this temperature until a solution was obtained (about 58 minutes), indicating the N-oxide was formed. The solution was then allowed to cool to about 55° C. and stirred for an additional 30 minutes.

(B) After cooling to room temperature, vanadyl sulfate (0.05 g, 29% water content) was added to the solution. After stirring for about 5 minutes, the color of the solution changed from blue to light green. Gas evolution began with a slow exotherm. When the temperature reached about 40° C., the exotherm greatly accelerated to 65° C. and cooling water was applied to maintain the solution at this temperature. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrate and solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 96.7%, and the selectivity to N-phosphonomethylglycine was 91.4%.

EXAMPLE 2

This Example illustrates the process of the present invention using a water-soluble ferrous salt to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

The procedure of Example 1 Step (A) was repeated. Then after the solution was allowed to cool to room temperature, ferrous sulfate (0.02 g) was added to the solution. Gas evolution was observed, and the temperature of the solution rose to 65° C. Cooling water was applied to keep the temperature below 70° C. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrate and solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 99.5%, and the selectivity to N-phosphonomethylglycine was 93.7%.

EXAMPLE 3

This Example illustrates the process of the present invention using zinc metal to convert N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

thyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

(A) To a 100 ml round bottomed glass flask was added water (37 ml), N-phosphonomethyliminodiacetic acid (14.0 g), 30% hydrogen peroxide (7.2 g) and ammonium dimolybdate tetrahydrate (0.32 g). The mixture was heated to 65° C. and maintained at this temperature until a solution was obtained (about 30 minutes), indicating the N-oxide was formed. The solution was then allowed to cool to 45° C. and stirred for 50 minutes.

(B) After cooling to room temperature, zinc metal powder (0.4 g) was added to the solution. Vigorous gas evolution was observed, and the temperature of the solution rose to 55° C. in about a 10-minute period. The reaction mixture was allowed to cool to room temperature, the solids were filtered, and the filtrate and solids were analyzed by HPLC. The conversion of N-phosphonomethyliminodiacetic acid was 91.0%, and the selectivity to N-phosphonomethylglycine was 93.8%.

EXAMPLE 4

This Example illustrates the use of copper metal, aluminum metal, and a water-soluble cuprous salt to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine.

The procedure of Example 3 Step (A) was repeated. After cooling to room temperature, small aliquots of the solution containing the N-phosphonomethyliminodiacetic acid-N-oxide were taken and placed in 25 ml beakers. To one aliquot was added a copper penny. To another aliquot was added aluminum foil. To a third aliquot was added a small amount of cuprous chloride, and to a fourth aliquot was added vanadium metal. In all cases, gas evolution was observed, indicating that the intermediate N-phosphonomethyliminodiacetic acid-N-oxide was converted to N-phosphonomethylglycine.

Although the invention has been described in terms of specified embodiments which are set forth in considerable detail, it should be understood that this is by way of illustration only, and that alternative embodiments and operating techniques will become apparent to those skilled in the art in view of the disclosure. Accordingly, modifications can be made without departing from the spirit of the described invention.

What is claimed is:

1. A process for producing N-phosphonomethylglycine which comprises oxidizing N-phosphonomethyliminodiacetic acid with a peroxide to form an intermediate N-phosphonomethyliminodiacetic acid-N-oxide, and then adding a catalytic amount of a ferrous salt to convert the intermediate to N-phosphonomethylglycine.

2. A process of claim 1 wherein the amount of catalyst to convert the intermediate N-phosphonomethyliminodiacetic acid-N-oxide to N-phosphonomethylglycine is between about 0.005 wt% and about 5 wt. %, based on the weight of the N-phosphonomethyliminodiacetic acid-N-oxide present.

3. A process of claim 2 wherein the amount of catalyst is between about 0.01 wt. % and about 2.0 wt. %.

* * * * *

[54] **PROCESS FOR PRODUCING
N-PHOSPHONOMETHYLGLYCINE SALTS**

[75] Inventor: John E. Franz, Crestwood, Mo.

[73] Assignee: Monsanto Company, St. Louis, Mo.

[21] Appl. No.: 926,681

[22] Filed: Jul. 21, 1978

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 753,232, Dec. 20, 1976, abandoned.

[51] Int. Cl.² C07F 9/38

[52] U.S. Cl. 260/501.12; 260/239 B;
260/326.11 R; 260/326.85; 260/502.5; 544/110;
544/78; 546/22

[58] Field of Search 260/239 B, 290 R, 293.87,
260/326.11 R, 326.85, 502.5, 501.12; 544/110,

78

[56]

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U.S. PATENT DOCUMENTS

3,950,402	4/1976	Franz	260/502.5
3,969,398	7/1976	Hershman	260/502.5
3,977,860	8/1976	Franz	260/239 B X

Primary Examiner—James O. Thomas, Jr.

Assistant Examiner—G. T. Breitenstein

Attorney, Agent, or Firm—Arnold H. Cole; Donald W. Peterson

[57]

ABSTRACT

Salts of N-phosphonomethylglycine are produced by forming a salt of N-phosphonomethyliminodiacetic acid with a salt-forming cation in an aqueous medium and then oxidizing the salt solution with an oxygen-containing gas in the presence of a platinum on activated carbon catalyst. The salts produced are useful as herbicides or plant growth regulants.

17 Claims, No Drawings

PROCESS FOR PRODUCING N-PHOSPHONOMETHYLGLYCINE SALTS

This application is a continuation-in-part of copending application Ser. No. 753,232, filed Dec. 20, 1976, now abandoned.

This invention relates to a method of producing certain mono and di salts of N-phosphonomethylglycine. More particularly, the invention is concerned with a method wherein such salts are produced by an oxidation reaction which provides high yields while minimizing or eliminating disadvantages of the prior art.

The preparation of such salts by reacting N-phosphonomethylglycine with the salt-forming cations of certain metals, ammonium or organic ammonium in aqueous solution is described in U.S. Pat. No. 3,977,860. Known procedures for preparing N-phosphonomethylglycine include oxidation of N-phosphonomethyliminodiacetic acid using such oxidizing agents as hydrogen peroxide, nitric acid, peroxyacetic acid and oxidation in aqueous media, e.g., water solutions using a free oxygen-containing gas and a noble metal catalyst such as platinum, palladium, rhodium, etc. as described in U.S. Pat. No. 3,950,402 or an activated carbon catalyst as described in U.S. Pat. No. 3,969,398. According to these patents, it is preferred to employ approximately saturated solutions of the N-phosphonomethyliminodiacetic acid in water at the temperature of reaction for ease of reaction and ease of recovery of the product. The saturated aqueous solution contains at most about 1 percent by weight of the acid at 25° C., about 4 percent by weight at 95° C. and about 10 percent by weight at 150° C. Such relatively low solubility of the acid in water severely restricts the amount of N-phosphonomethyliminodiacetic acid which can be charged and oxidized in a batch reaction system to form the desired N-phosphonomethylglycine. In order to recover the N-phosphonomethylglycine from the aqueous solution, water has to be distilled off and this requires the expenditure of considerable heat energy.

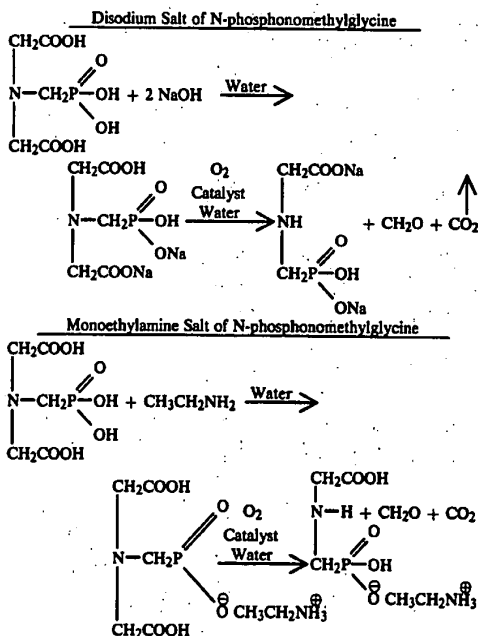
It has now been found that the salts of N-phosphonomethylglycine can be readily prepared using a single aqueous reaction system in which a salt of N-phosphonomethyliminodiacetic acid is oxidized by a molecular oxygen-containing gas in the presence of a noble metal oxidation catalyst. The mono and di salts of N-phosphonomethylglycine which are produced by this method are those wherein the salt-forming cation is selected from the group consisting of the cations of alkali metals, alkaline earth metals, ammonium and organic ammonium provided that when the organic group is aryl, the ammonium salt is a primary amine salt.

The term "alkali-metal" encompasses lithium, sodium, potassium, cesium and rubidium, and the term "alkaline earth metal" includes beryllium, magnesium, calcium, strontium and barium.

The organic ammonium salts of the above type are those prepared from low molecular weight organic amines, i.e., having a molecular weight below about 300, and such organic amines include: the alkyl amines, alkylene amines and alkanol amines containing not more than 2 amine groups, such as methylamine, ethylamine, n-propylamine, isopropylamine, n-butylamine, isobutylamine, sec-butylamine, n-amylamine, isoamylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, undecylamine, dodecylamine, tridecylamine, tetradecylamine, pentadecylamine, hexa-

decylamine, heptadecylamine, octadecylamine, methylethylamine, methylisopropylamine, methylhexylamine, methylnonylamine, methylpentadecylamine, methyloctadecylamine, ethylbutylamine, ethylheptylamine, ethyloctylamine, hexylheptylamine, hexyloctylamine, dimethylamine, diethylamine, di-n-propylamine, diisopropylamine, di-n-amylamine, diisoamylamine, dihexylamine, diheptylamine, dioctylamine, trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-secbutylamine, tri-n-amylamine, ethanamine, n-propanolamine, isopropanolamine, diethanamine, N,N-diethylethanamine, N-ethylpropanolamine, N-butylethanamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl-2-amine, di-butenyl-2-amine, n-hexenyl-2-amine and propylenediamine; primary aryl amines such as aniline, methoxyaniline, ethoxyaniline, o,m,p-toluidine, phenylenediamine, 2,4,6-tribromoaniline, benzidine, naphthylamine, o,m,p-chloroaniline, and the like; and heterocyclic amines such as pyridine, morpholine, piperidine, pyrrolidine, indoline, azepine and the like.

In the aforescribed aqueous reaction system, the charged reactants initially form the mono or di salts of N-phosphonomethyliminodiacetic acid (depending on the stoichiometry), and these salts as formed are then oxidized to N-phosphonomethylglycine salts as indicated below for the disodium salt and the monoethylamine salt, respectively.



By the term "molecular oxygen-containing gas", as employed herein, is meant any gas containing molecular oxygen with or without diluents which are non-reactive with the oxygen or with the reactant or product under the conditions of reaction. Examples of such gases are air, oxygen, oxygen diluted with helium, argon, nitrogen, or other inert gas, oxygen-hydrocarbon mixtures and the like. It is preferred to employ gases containing 20 or more percent by weight molecular oxygen and even more preferred to employ gases containing 90 or

more percent by weight molecular oxygen. It is, of course, obvious to those of ordinary skill in the art that when molecular oxygen-containing gases containing other inert gases are employed, the pressures should be increased to insure adequate partial pressures of oxygen in the system to maintain a sufficient rate of reaction.

The amount of the molecular oxygen-containing gas employed can vary over wide ranges. It is, of course, obvious to those skilled in the art that the best yields of the N-phosphonomethylglycine salts are produced when at least stoichiometric amounts of oxygen are employed. In most instances for ease of reaction and best yield of the final product, the amount of oxygen employed would ordinarily be at least $\frac{1}{2}$ mole of oxygen for each mole of N-phosphonomethyliminodiacetic acid salt. In actual practice, the amount of oxygen employed will be from $\frac{1}{2}$ to 1 or more moles for each mole of the N-phosphonomethyliminodiacetic acid salt since the efficiency of the oxygen utilization is usually less than 100 percent.

The noble metal oxidation catalyst used in the method of this invention is platinum, and such metal is supported on an activated carbon substrate. The activated carbon supports which can be employed are commercially available under a wide variety of trade names, and the manner in which the metal is placed on the substrate is well understood in the art. Many of the useful activated carbon supports are described in detail in U.S. Pat. No. 3,969,398.

In conducting the process of this invention, it is preferred to employ approximately saturated solutions of the N-phosphonomethyliminodiacetic acid salt in water at the temperature of reaction for ease of reaction and ease of recovery of the product, N-phosphonomethylglycine salt. The temperature employed in carrying out the process of this invention should be sufficient to initiate the reaction and to sustain the reaction once initiated. Temperatures of from about 25° C. to 150° C. or even higher are usually satisfactory. As those skilled in the art would realize, at lower temperatures the rate of reaction may be undesirably slow and, therefore, temperatures of at least 75° C. are preferred and even more preferred are temperatures in the range of about 90° C. to 150° C.

The oxidation reaction is conducted at superatmospheric pressures, and it is preferred that a range of about 1.5 to 5 Kg/cm² be employed. Such pressures enable the reaction to proceed to substantial completion in a relatively few hours. Use of pressures greater than 5 Kg/cm² is feasible providing the reaction vessel is properly selected.

As noted above, the related oxidation processes of the prior art employ N-phosphonomethyliminodiacetic acid as the starting material, and the very low aqueous solubility of this acid severely restricts the quantity of product which can be obtained from any given volume of water. In addition, removal of the large amounts of water by distillation in order to isolate said product requires a correspondingly large expenditure of energy.

Another problem in the prior art processes is the presence of formaldehyde which is a co-product in the oxidation reaction. This co-product must also be removed by distillation, and it is then subjected to aerobic

oxidation before disposal in order to comply with environmental regulations. The presence of the formaldehyde co-product during the oxidation reaction is also undesirable since it contributes to and accelerates the formation of by-products such as N-methyl-N-phosphonomethylglycine and methylaminomethylphosphonic acid which are difficult to separate from the desired product. Although azeotropic distillation of the formaldehyde from the reaction mixture could be employed during the reaction itself, this would require added equipment and would not resolve the matter of subsequent disposal.

In accordance with the present invention, it has been found that the disadvantageous features of the prior art can be minimized or eliminated by the oxidation of a salt of N-phosphonomethyliminodiacetic acid using a platinum on activated carbon catalyst to yield a salt of N-phosphonomethylglycine.

The test procedures hereinafter described were employed to demonstrate the performance of the process of this invention. It should be understood that the specific details of each test are illustrative only and should not be construed as a limitation upon the scope of the invention. For comparison purposes, these test procedures were also carried out with various catalysts of the prior art.

For each of the runs tabulated below, the reaction vessel was a thick walled, 500 ml. glass bottle mounted on a Parr shaker. The bottle included an outer explosion shield which was wrapped with electrical heating tape, and the heating was controlled by a Variac transformer. A metal dial thermometer was inserted through a hole in the explosion shield and measured "outside" temperatures in terms of a relatively narrow range. The temperatures inside the reaction vessel itself were considered to be about 10° C. below said "outside" temperatures when the latter were measured in the 90°-110° C. range.

In each run, measured amounts of the N-phosphonomethyliminodiacetic acid and the base or cation contributor were added to 100 ml. of hot water in the bottle, the catalyst was added, and the reaction mixture was heated to a selected temperature. The bottle was pressurized with oxygen to a gauge pressure of 2.11 Kg/cm², bled down to atmospheric pressure, repressurized to the desired pressure and agitated on the shaker during the reaction period. Reaction pressure was carefully monitored, and after each increase of 0.35 Kg/cm² over the desired pressure, the reactor was bled to zero gauge pressure and then repressurized to the original starting level. This prevented an excessive accumulation of the CO₂ formed during the oxidation.

The course of the reaction was followed by periodic centrifugation of a small volume of the reaction mixture, acidification of the resultant clear solution with an equal volume of concentrated HCl, and determination of the proton NMR spectrum. In the tabulation of test results, the "% Unreacted Salt" in the product is based on said NMR analysis and indicates the degree of completion of the reaction in the specified time. Where "% Yield" is given, this indicates the amount of N-phosphonomethylglycine salt determined by U.V. analysis. All parts and percentages below are by weight unless otherwise stated.

Run	Starting Materials (gm./100 ml H ₂ O)			Reaction Conditions			Reaction Product		
	Acid	Base	Catalyst	hrs.	Kg/cm ²	° C.	% Unreacted		Comments
							Salt	Yield	
A	12.0	IPA 3.15	5% Pt/C 0.5	3.0	2.11	102-109	9	—	Formaldehyde = 30% theory By-product I = 2-3%
B	12.0	IPA 3.15	5% Pt/C 1.0	1.5	2.11	102-110	0	—	Formaldehyde = 32% theory By-product I = trace Very clean NMR
C	18.0	IPA 4.8	5% Pt/C 1.5	2.25	2.11	109-111	1	—	Formaldehyde = 20% theory By-product I = small amount Clean NMR
D	24.0	IPA 6.3	5% Pt/C 2.0	2.5	2.11-2.81	108-114	6	—	Formaldehyde = 14% theory By-product I = 3%
E	12.0	IPA 3.15	5% Pt/C 1.0	1.75	2.11	106-110	0	98	Formaldehyde = 30% theory By-product I = trace Very clean NMR
F	18.0	IPA 4.5	5% Pt/C 2.0	2.2	2.11	105-111	0	94	Formaldehyde = 16% theory By-product I = trace Very clean NMR
G	22.5	IPA 5.7	5% Pt/C 3.0	2.2	2.11	105-112	0	92	Formaldehyde = 12% theory By-product I = trace Very clean NMR
H	27.0	IPA 6.8	5% Pt/C 3.0	2.5	2.11	105-111	0	89	Formaldehyde = 10% theory By-product I = small amount By-product II = small amount Clean NMR
I	4.5	IPA 1.15	5% Pt/C 0.5	1.25	2.11	104-110	0	95	Formaldehyde = 25% theory No obvious by-products Very clean NMR
J	12.0	TMA 11.5	5% Pt/C 1.0	1.25	2.11	104-112	0	95	Formaldehyde = 1% theory Very clean NMR
K	13.5	30% NH ₃ 1.0	5% Pt/C 1.5	1.5	2.11	104-106	0	92	Formaldehyde = 20% theory Very clean NMR
L	12.0	25% DMA 9.0	5% Pt/C 1.0	1.25	2.11	104-110	0	93	Formaldehyde = 25% theory Clean NMR
M	12.0	86% KOH 3.0	5% Pt/C 1.0	1.5	2.11	104-115	0	94	Formaldehyde = 1% theory By-product II = small amount Very clean NMR
N	13.5	86% KOH 3.7	5% Pt/C 1.5	1.0	2.11	104-112	0	96.5	Formaldehyde = 3-4% theory Very clean NMR
O	4.5	86% KOH 1.3	5% Pt/C 1.0	17.0	2.11	24-26 26-30	0	—	No formaldehyde Clean NMR
P	1.15	86% KOH 0.55	5% Pt/C 0.25	3.0	2.11	25	45	—	Formaldehyde = 15-20% theory Clean NMR
Q	12.0	IPA 3.15	5% Rh/C 0.5	2.0	2.11	104-109	11	—	Formaldehyde = 70% theory By-product I = 5-8%
R	13.5	IPA 3.35	5% Rh/C 1.5	0.75	2.11	104-112	0	88	Formaldehyde = 25% theory By-product I = 2-3% Light yellow filtrate
S	13.5	IPA 3.35	5% Rh/C 1.5	1.0	2.11	109-110	0	—	Formaldehyde = 34% theory By-product I = 3-4% By-product II = small amount Yellow filtrate
T	12.0	IPA 3.15	5% Pd/C 0.5	3.0	2.11	102-109	5	—	Formaldehyde = 36% theory By-product I = 10% Yellow filtrate
U	13.5	IPA 3.35	5% Pd/C 1.5	1.0	2.11	104-106	0	84	Formaldehyde = 82% theory By-product I = 2.5% By-product II = trace Yellow filtrate
V	4.5	IPA 1.15	5% Pt/Al ₂ O ₃ 0.5	2.5	2.11	103-109	43	—	Formaldehyde = 5% theory Clean NMR
W	6.0	IPA 1.6	F-1A 0.5	2.0	2.11	90-95	0	97	Formaldehyde = 100% theory By-product I = trace Very clean NMR
X	12.0	IPA 3.15	F-1A 0.6	2.0	2.11	102-109	8	—	By-product I = 5-8%
Y	12.0	IPA 3.15	NORIT 1.0	2.0	2.11	106-108	0	67	By-product I = significant amount By-product II = significant amount
Z	4.5	IPA 1.15	NORIT 1.15	1.25	2.11	104-110	0	93	Formaldehyde = 100% theory By-product II = trace
AA	12.0	IPA 3.05	F-1C 1.0	2.0	2.11	104-112	0	65	By-product I = extensive By-product II = extensive Yellow filtrate
BB	13.2	IPA 3.35	NORIT 1.5	1.07	2.11	104-109	2	78	By-product I = significant amount By-product II = significant

-continued

Run	Starting Materials (gm./100 ml H ₂ O)			Reaction Conditions			Reaction Product		
	Acid	Base	Catalyst	hrs.	Kg/cm ²	' C.	% Unreacted Salt	% Yield	Comments
CC	13.5	IPA 3.35	F-6 1.5	3.0	2.11	104-110	46	—	Slightly yellow filtrate Formaldehyde = 22% theory By-product I = 3.5%
DD	13.5	IPA 3.35	F-7 1.5	3.0	2.11	104-110	29	—	Formaldehyde = 70% theory By-product I = 9% Light yellow filtrate
EE	13.5	IPA 3.35	F-8 1.5	2.0	2.11	104-112	20	—	Formaldehyde = 70% theory By-product I = 6% Light yellow filtrate
FF	13.5	IPA 3.35	F-9 1.5	2.0	2.11	104-112	15	—	Formaldehyde = 90% theory By-product I = 5% Slight yellow filtrate
GG	13.5	IPA 3.35	F-10 1.5	1.0	2.11	104-112	0	79	Formaldehyde = 85% theory By-product I = 6% Slightly yellow filtrate Clear NMR
HH	13.5	86% KOH 3.7	NORIT 1.5	1.0	2.11	104-109	0	79	Formaldehyde = 75% theory By-product I = 6% By-product II = trace

In Run P, the starting materials were added to 25 ml. of hot water in a 100 ml. glass bottle. As regards the base employed, IPA designates isopropylamine, TMA designates trimethylamine and DMA designates dimethylamine. By-product I is N-methyl-N-phosphonomethylglycine, and by-product II is methylaminomethylphosphonic acid. The noble metal catalysts employed are all commercial products, and the same is true of the activated carbon catalyst Norit A. The various F designated catalysts are all activated carbons prepared as described below.

F-1A

Norit A (10 gm.), distilled water (100 ml.) and conc. HCl (100 ml.) were refluxed for 40 hours, cooled to room temperature and filtered. The residue was washed with distilled water and then with very diluted ammonia until the filtrate was neutral. The product was washed once more with a large volume of water and then dried at 100° C. for 1.5 days.

F-1C

Norit A (100 gm.), distilled water (200 ml.) and conc. HCl (100 ml.) were refluxed with stirring for 40 hours, cooled to room temperature and filtered. The product was washed and dried as described for F-1A. This product (21 gm.), distilled water (100 ml.) and conc. HCl (100 ml.) were refluxed with agitation for 40 hours, filtered hot and the residue washed with a large volume of boiling distilled water until the filtrates were neutral. The product was dried to constant weight at 115° C.

F-6

A ground mixture of sucrose (50 gm.) and urea (5 gm.) was gradually pyrolyzed in a porcelain crucible and the residue annealed at a red heat for 50 minutes. The grey-black product resembled graphite more than charcoal.

F-7

A mixture of annealed lampblack (7.5 gm.), sublimed ferric chloride (1.5 gm.), urea (5 gm.) and water (25 ml.) was concentrated at reduced pressure and the residue ground to a powder. The latter was annealed in a porcelain crucible at a red heat for 30 minutes. The cooled product was washed repeatedly with a mixture of 250

ml. of boiling water and 25-50 ml. of conc. HCl until the filtrates were colorless. The material was then washed with boiling water until the filtrates were neutral. The product was dried at 110° C. for 3 days.

F-8

A ground mixture of sucrose (50 gm.), urea (5 gm.) and sublimed ferric chloride (1.5 gm.) was gradually pyrolyzed and the residue annealed at a red heat for 30 minutes. The product was ground to a powder and extracted with hot dilute HCl until the filtrates were colorless. The residue was then washed with boiling water until the filtrates were neutral and finally dried to constant weight at 110° C.

F-9

F-8 carbon catalyst (3 gm.) was extracted with conc. HCl until the filtrates were colorless. The initial filtrates are yellow due to ferric chloride formed from iron which is not extracted with hot dilute HCl. The material was then washed with a large volume of boiling water until neutral and dried to constant weight at 110° C.

F-10

Norit A (3 gm.) was extracted with conc. HCl, washed and dried as described for F-9 catalyst.

The data presented in the table demonstrates the several advantages of the present invention. Using the low payloads which the prior art processes suggest, a comparison of Run I with Runs W and Z show the yields with the instant platinum on carbon catalyst are about the same as those with the activated carbons alone. However, said platinum on carbon catalyst provides concurrent oxidation of the formaldehyde co-product as it is formed. Thus the time and expense required to remove said co-product from the final reaction product is significantly reduced.

When the payloads are increased by a factor of two or three, Runs E, J, L and N show that the platinum on carbon catalyst continues to give a yield of desired product at a 90% or greater level. However, a similar increase in payload with an activated carbon catalyst gives yields below 80% as shown in Runs Y, AA and

HH. Further, since the activated carbon catalysts already do not provide for concurrent oxidation of the formaldehyde, the presence of the latter causes increased production of the undesirable by-products. Runs F, G and H show that still higher payloads can be employed with the platinum on carbon catalyst without any adverse effect on the % yield obtained. In addition, these higher payload runs also show relatively low levels of formaldehyde co-product with minimal by-product formation.

Returning to the increased payload Runs E, J, L and N with the platinum on carbon catalyst of this invention, it can be seen that they also compare favorably with corresponding Runs R and U which employed rhodium and palladium, respectively, on carbon. The other noble metal runs are characterized by somewhat reduced yields, along with some increase in co-product and by-product formation. The use of rhodium or palladium also gives rise to a discolored yellow filtrate in the product whereas the runs with the platinum on carbon catalyst regularly gives a colorless filtrate.

While the invention has been described herein with regard to certain representative examples for the purpose of illustrating its practice, those skilled in the art will readily recognize the variations and modifications which can be made without departing from the spirit and scope thereof.

What is claimed is:

1. Process for preparing a mono or di salt of N-phosphonomethylglycine wherein the salt-forming cation is selected from the group consisting of cations of alkali metals, alkaline earth metals, ammonium and organic ammonium, provided that when the organic group is aryl, the ammonium salt is a primary amine salt, which comprises contacting, at superatmospheric pressure, an aqueous solution of a corresponding mono or di salt of N-phosphonomethyliminodiacetic acid with an oxygen-containing gas in the presence of an oxidation catalyst which is platinum on activated carbon.

2. Process as defined in claim 1 wherein said superatmospheric pressure is at least about 1.5 Kg/cm².

3. Process as defined in claim 1 wherein said contacting is carried out at a temperature of from about 25° C. to 150° C.

4. Process as defined in claim 3 wherein said contacting is carried out at a temperature of at least about 90° C.

5. Process as defined in claim 1 wherein said salt-forming cation is alkali metal.

6. Process as defined in claim 1 wherein said salt-forming cation is said organic ammonium.

7. Process as defined in claim 1 wherein said contacting is carried out with the monoisopropylamine salt of N-phosphonomethyliminodiacetic acid.

8. Process as defined in claim 1 wherein said contacting is carried out with the mono(dimethylamine)salt of N-phosphonomethyliminodiacetic acid.

9. Process as defined in claim 1 wherein said contacting is carried out with the monopotassium salt of N-phosphonomethyliminodiacetic acid.

10. Process as defined in claim 1 wherein said contacting is carried out with the mono(trimethylamine)salt of N-phosphonomethyliminodiacetic acid.

11. Process as defined in claim 1 wherein said contacting is carried out with the monoammonium salt of N-phosphonomethyliminodiacetic acid.

12. Process as defined in claim 1 wherein said superatmospheric pressure is at least about 1.5 Kg/cm², and said contacting is carried out at a temperature of from about 90° C. to 150° C.

13. Process as defined in claim 12 wherein said contacting is carried out with the monoisopropylamine salt of N-phosphonomethyliminodiacetic acid.

14. Process as defined in claim 12 wherein said contacting is carried out with the mono(dimethylamine)salt of N-phosphonomethyliminodiacetic acid.

15. Process as defined in claim 12 wherein said contacting is carried out with the monopotassium salt of N-phosphonomethyliminodiacetic acid.

16. Process as defined in claim 12 wherein said contacting is carried out with the mono(trimethylamine)salt of N-phosphonomethyliminodiacetic acid.

17. Process as defined in claim 12 wherein said contacting is carried out with the monoammonium salt of N-phosphonomethyliminodiacetic acid.

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